

Advances in

**ORGANOMETALLIC
CHEMISTRY**

VOLUME 17

CATALYSIS AND ORGANIC SYNTHESSES

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ORGANOMETALLIC CHEMISTRY

VOLUME 17

Catalysis and Organic Syntheses

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Advances in Organometallic Chemistry

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Catalysis and Organic Syntheses

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Preface

This volume of *Advances in Organometallic Chemistry* is concerned exclusively with the involvement of metal compounds in catalysis and organic synthesis. We have collected together ten chapters on these topics so as to provide in one volume a survey of the growing importance of organometallics in industrial processes and laboratory syntheses. It is impossible to provide complete coverage of the subject within the confines of a single volume of necessarily limited length. Nevertheless, we believe that our contributors have presented ample evidence of what many regard as the most significant growth area of organometallic chemistry and one of vast technological importance.

Several articles on these topics have appeared in earlier volumes. For the convenience of readers they are listed here. In addition, articles on Ziegler–Natta catalysis and on organolithium compounds in diene polymerization are planned for the next volume of this serial publication.

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Hydroformylation

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I**INTRODUCTION**

Hydroformylation is the general term applied to the reaction of an olefin with carbon monoxide and hydrogen to form an aldehyde. Because unsaturated hydrocarbons, especially C_2 – C_4 olefins, are important building blocks in the petrochemical industry, and because oxygenated products such as alcohols or acids are industrially important chemicals, the hydroformylation reaction has been the subject of intensive investigation. At the present time, about 8–10 billion pounds of aldehydes or derivatives thereof are produced annually by hydroformylation of an olefin substrate, with butyraldehyde from propylene being the largest single primary prod-

uct at a volume of about 6 billion pounds per year. The process is the most important industrial synthesis which uses metal carbonyl catalysts (1).

The hydroformylation reaction was discovered by Otto Roelen in 1938 (2, 3) while investigating the influence of olefins on the Fischer-Tropsch reaction (1). Particularly in commercial publications, it has been termed the "oxo" reaction; the more proper term, "hydroformylation," was proposed by Adkins (4).

The reaction does not proceed in the absence of catalysts. As the contemporary Fischer-Tropsch catalysts were heterogeneous, the first hydroformylation catalyst was a solid (66% silica, 30% cobalt, 2% thorium oxide, and 2% magnesium oxide). Only later was the conclusion reached and proved (5) that the actual catalytic species is homogeneous.

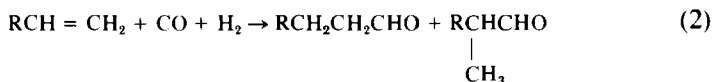
The hydroformylation reaction has been the subject of excellent reviews (for example 1, 6-8); therefore, the object of this particular treatise is not to provide comprehensive coverage of all aspects. The basic chemistry is presented, along with recent developments of interest as reported in the literature, although not in chronological order. Stereochemical studies (6) are included only when pertinent to another point under consideration. Carbonylations or hydrocarboxylation reactions which produce ketones, esters, acids, esters, or amides are not included (1). Also not included is the so-called "Reppe" synthesis, which is represented by Eq. (1).



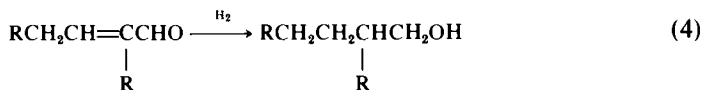
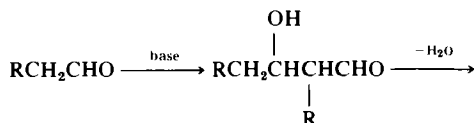
II

COMMERCIAL UTILIZATION

The primary product of hydroformylation, as it is usually practiced, consists of aldehydes with one more carbon atom than the olefin substrate.



These aldehydes can then be used to produce a variety of useful derivatives; the aldehydes themselves have minimum utility. The major derivatives are alcohols, formed either by direct hydrogenation [Eq. (3)], or by an aldol condensation followed by hydrogenation [Eq. (4)].



As noted previously, the major alcohol of commerce produced by hydroformylation is *n*-butanol, whose principal utility is found in solvent applications. The major alcohol formed through the aldol sequence is 2-ethylhexanol, again derived from propylene [Eq. (4), R = CH₃CH₂—]. This alcohol is esterified with phthalic anhydride to form dioctyl phthalate (DOP), the utility of which is for plasticizing polyvinyl chloride resins. Processes have been described (9, 10) which combine the hydroformylation, aldol, and hydrogenation steps into a single process; however, these have not gained widespread industrial usage at this time. Alcohols of higher chain length, principally C₁₃–C₁₅, are utilized as detergents.

Other derivatives formed from the aldehydes are acids and amines, produced by oxidation and reductive amination, respectively [Eqs. (5), (6)].



The volume of usage for these materials is small, relative to alcohols.

The need for higher product specificity and milder reaction conditions (see also Section IX) has led to extensive research in hydroformylation technology. This research, as reported in technical journals, patent literature, and commercial practice has been primarily concerned with catalysis by rhodium, in addition to the traditional cobalt, and with catalyst modification by trialkyl or triaryl phosphines. These catalyst systems form the basis for the major portion of the discussion in this chapter; some other catalyst systems are discussed in Section VIII.

Rhodium has an activity 10⁴ times greater than that of cobalt (8).

III

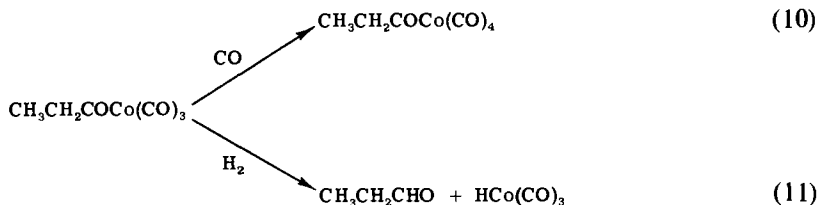
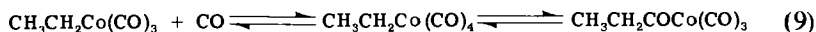
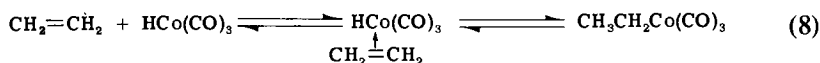
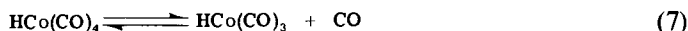
REACTION MECHANISM

After it was recognized that the hydroformylation reaction is catalyzed by a soluble species, HCo(CO)₄ was proposed as the catalyst (11). Sub-

sequent proposals regarding the mechanism were made by Wender *et al.* (12), and Natta *et al.* (13, 14) made some important observations concerning the kinetics of the reaction. The first-order dependence on hydrogen pressure is balanced by an inverse first-order dependence on carbon monoxide partial pressure. Therefore, the reaction rate is nearly independent of total pressure. The reaction is first order in olefin and first order in cobalt at higher carbon monoxide partial pressures.

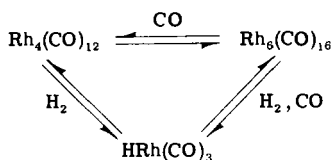
Another important line of investigation concerned the "carbonyl insertion" reaction, which was best defined in manganese chemistry (15, 16) and extended to acylcobalt tetracarbonyls by Heck and Breslow. The "insertion" may be through three-membered ring formation or by nucleophilic attack of an alkyl group on a coordinated CO group.

The mechanism offered by Heck and Breslow (17, 18) has been the one most accepted as representing the probable reaction course. This is outlined in Eqs. (7)–(11):

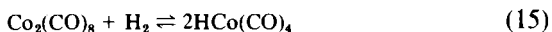
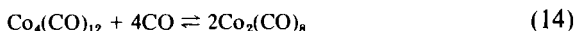
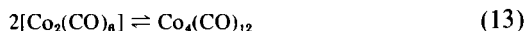


This scheme is shown with ethylene as the olefin substrate. If the olefin is substituted, i.e., $\text{RCH}=\text{CH}_2$, the possibility exists for the formation of the isomers $\text{RCH}_2\text{CH}_2\text{Co}(\text{CO})_3$ or $\text{RCH}(\text{CH}_3)\text{Co}(\text{CO})_3$ in Eq. (8). These isomers, which result from the insertion of olefin into the $\text{Co}-\text{H}$ bond, then produce the isomeric aldehydes $\text{RCH}_2\text{CH}_2\text{CHO}$ and $\text{RCH}(\text{CH}_3)\text{CHO}$. The understanding of the factors which determine these pathways and control the desired product, has been the motivation for much study.

For rhodium carbonyls, the reaction follows a similar pathway except for the complication of equilibria involving the presumed intermediate $[\text{HRh}(\text{CO})_3]$ (19). A similar equilibrium was postulated at an early date by Natta *et al.* (14) in order to explain the half-order dependence on



carbon monoxide at low partial pressures in the cobalt-catalyzed reaction [Eqs. (12)–(15)].



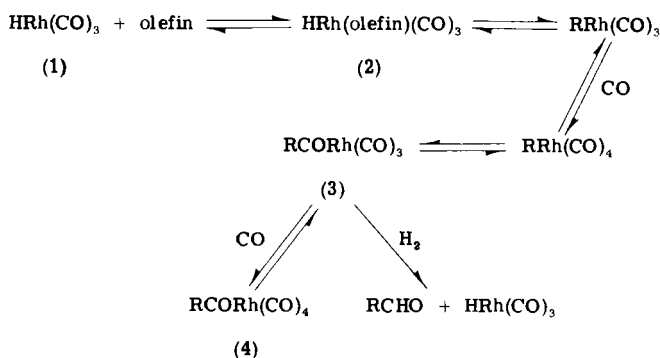
The formation of multinuclear clusters is much more favorable for rhodium than for cobalt. Additional evidence was obtained in comparative hydroformylation rate studies of 1-heptene and of cyclohexene at 75°C and 150 atm 1/1 H₂/CO (19). For the acyclic olefin the kinetics followed the kinetic expression (except at low olefin):

$$\frac{d(\text{aldehyde})}{dt} = k_{\text{obs}}[\text{heptene}]^0[\text{Rh}][P_{\text{H}_2}][P_{\text{CO}}]^{-1}$$

But for the less reactive cyclic olefin, the expression became, with $\text{Rh}_4(\text{CO})_{12}$ as the catalyst,

$$\frac{d(\text{aldehyde})}{dt} = k_{\text{obs}}[\text{cyclohexene}][\text{Rh}]^{1/4}[P_{\text{H}_2}]^{1/2}[P_{\text{CO}}]^0 \quad (16)$$

Both these results were explained in terms of the following reaction sequence:



For 1-heptene, the rate-determining step was concluded to be the

hydrogenation of the acyl intermediate (3) to aldehyde and $\text{HRh}(\text{CO})_3$ (1). The $\text{Rh}_4(\text{CO})_{12}$ which was added as catalyst was transformed after a short induction period, the 1-heptene reacted rapidly, and the acyl derivative, not $\text{Rh}_4(\text{CO})_{12}$, was seen in high-pressure infrared spectra (19, 20).

In the case of cyclohexene, no change was noted in the initial spectrum of $\text{Rh}_4(\text{CO})_{12}$ at temperatures below 100°C and not too long reaction times. This agrees with the kinetic data in that the reaction of the olefin with $\text{HRh}(\text{CO})_3$ is the rate-limiting step with this less reactive olefin, and that the $\text{HRh}(\text{CO})_3$ is in equilibrium with $\text{Rh}_4(\text{CO})_{12}$. At higher temperatures and/or longer reaction times, $\text{Rh}_6(\text{CO})_{16}$ was seen in the infrared spectrum and the reaction was slower. The thermodynamically favored cluster under these conditions is $\text{Rh}_6(\text{CO})_{16}$, and the equilibrium would be less favorable for formation of $\text{HRh}(\text{CO})_3$.

Most hydroformylation investigations reported since 1960 have involved trialkyl or triarylphosphine complexes of cobalt and, more recently, of rhodium. Infrared studies of phosphine complex catalysts under reaction conditions as well as simple metal carbonyl systems have provided substantial information about the postulated mechanisms. Spectra of a cobalt 1-octene system at 250 atm pressure and 150°C (21) contained absorptions characteristic for the acyl intermediate $\text{C}_8\text{H}_{17}\text{COCO}(\text{CO})_4$ (2103 and 2002 cm^{-1}) and $\text{Co}_2(\text{CO})_8$. The amount of acyl species present under these steady-state conditions increased with a change in the CO/H_2 ratio in the order $3/1 > 1/1 > 1/3$. This suggests that for this system under these conditions, hydrogenolysis of the acyl cobalt species is a rate-determining step.

However, when a less active olefin (e.g., diisobutylene or cyclohexene) or a liganded system ($\text{Bu}_3\text{P}/\text{Co} = 2/1$, 80 atm CO/H_2 , 190°C) was used, the hydrido species, e.g., $\text{HCo}(\text{CO})_3\text{PBU}_3$, predominated throughout the reaction. The author concluded that in *slower* systems, initial interaction of the olefin with the hydrido species $\text{HCo}(\text{CO})_3\text{L}$ could be the rate-determining step. These results are complementary to those discussed (*vide supra*) for the rhodium carbonyl catalysis.

It should be noted that these results with the cobalt carbonyl phosphine catalysts may not apply over a wide range of conditions. At milder conditions of lower temperature and low catalyst concentration, the conversion of $\text{Co}_2(\text{CO})_8$ to $\text{HCo}(\text{CO})_3\text{PR}_3$ is only partially completed, even with up to 5/1 ratios of P/Co (22).

In a different type of investigation, the individual steps of the hydroformylation of ethylene by $\text{HIr}(\text{CO})_3[\text{P}(\text{iso-C}_3\text{H}_7)_3]$ were characterized by high-pressure infrared studies (23). This particular catalyst was chosen because of its relative stability. The series of spectra in Figs. 1–3 show the changes that occurred on treating $\text{HIr}(\text{CO})_3(\text{P-i-Pr}_3)$ with 200 psi of ethylene at 50°C (Fig. 1), and on treating the resultant $\text{C}_2\text{H}_5\text{COIr}(\text{CO})_3(\text{P-}$

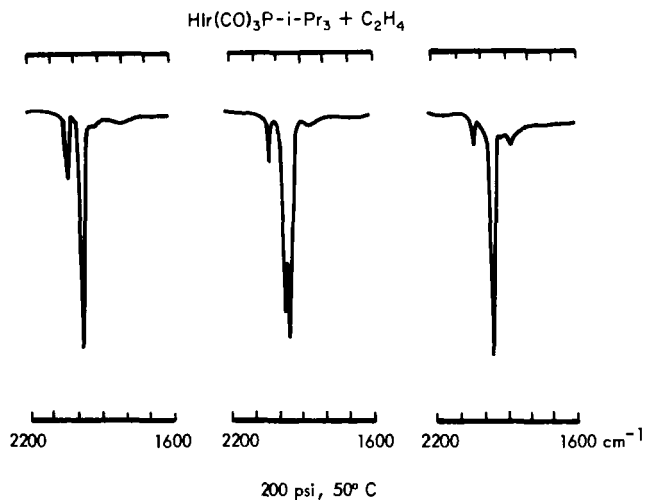


FIG. 1. Infrared spectral changes during the reaction of $\text{HIr}(\text{CO})_3\text{P-i-Pr}_3$ and ethylene in heptane. Reprinted with permission from *J. Organometal. Chem.* **94**, 303 (1975). Copyright by Elsevier Sequoia S. A.

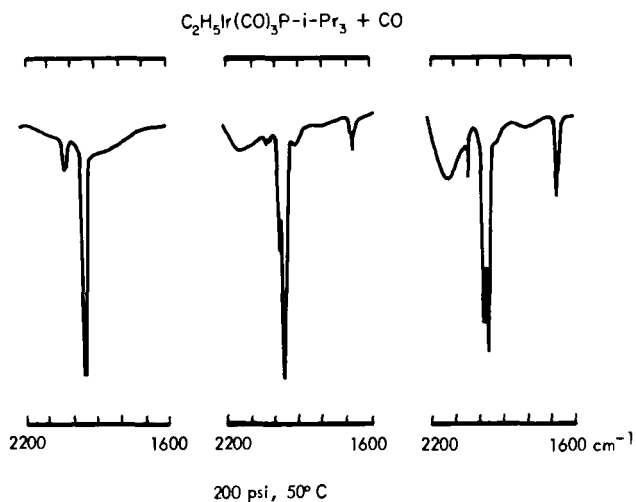


FIG. 2. Infrared spectral changes during the reaction of $\text{C}_2\text{H}_5\text{Ir}(\text{CO})_3\text{P-i-Pr}_3$ and carbon monoxide in heptane. Reprinted with permission from *J. Organometal. Chem.* **94**, 303 (1975). Copyright by Elsevier Sequoia S. A.

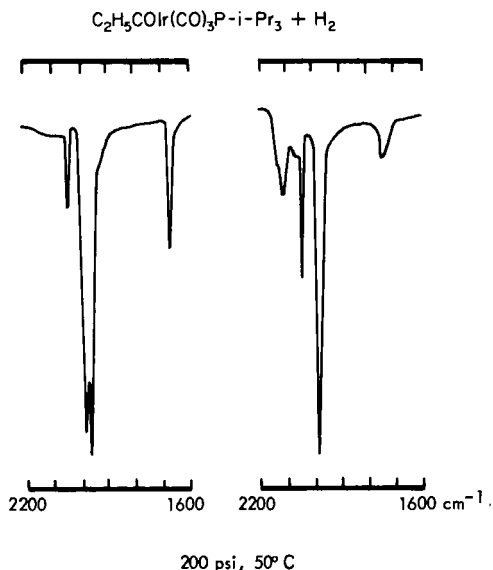


FIG. 3. Infrared spectral changes during the reaction of $\text{C}_2\text{H}_5\text{COIr}(\text{CO})_3\text{P-i-Pr}_3$ and hydrogen. Reprinted with permission from *J. Organometal. Chem.* **94**, 303 (1975). Copyright by Elsevier Sequoia S. A.

i-Pr_3) with 200 psi of H_2 at 50°C . All stages of the sequence $\text{HIr}(\text{CO})_3(\text{PR}_3) \rightarrow \text{C}_2\text{H}_5\text{Ir}(\text{CO})_3(\text{PR}_3) \rightarrow \text{C}_2\text{H}_5\text{COIr}(\text{CO})_3\text{PR}_3 \rightarrow \text{C}_2\text{H}_5\text{CHO} + \text{HIr}(\text{CO})_3\text{PR}_3$ are spectroscopically isolated and shown to be actual intermediates. The individual absorbances are given in Table I.

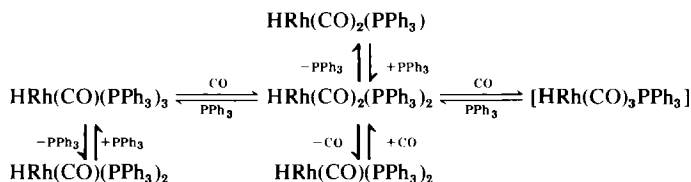
For the phosphine-substituted cobalt carbonyl hydroformylations, it is probable that the mechanism follows the pathway of Heck and Breslow (17, 18), although the possibility of an associative mechanism has been raised (7). The increased stability of the $\text{HCo}(\text{CO})_3\text{PR}_3$ complexes toward loss of CO was cited as being suggestive of a nondissociative pathway.

The studies of Wilkinson *et al.* during the late 1960's (24–27) concerning

TABLE I
INFRARED SPECTRA OF IRIUM COMPLEXES (23)

$\text{HIr}(\text{CO})_3(\text{P-i-Pr}_3)$	$\text{C}_2\text{H}_5\text{Ir}(\text{CO})_3(\text{P-i-Pr}_3)$	$\text{C}_2\text{H}_5\text{COIr}(\text{CO})_3(\text{P-i-Pr}_3)$
2038 m	2030 m	2041 w
	2025 w	
1970 vs	1957 s	1978 s
	1954 s	1959 s
1933 w	1920 vw	
		1671 m

the triphenylphosphine-modified rhodium systems led them to propose both dissociative and associative mechanisms, as outlined in Figs. 4 and 5. The complex $\text{HRh}(\text{CO})_2(\text{PPh}_3)_2$ was selected as the key intermediate, even though an equilibrium between several species may exist in solution (28).



This selection was substantiated by the observation (29) that, if $\text{HRh}(\text{CO})(\text{PPh}_3)_2$ and $\text{HRh}(\text{CO})_2(\text{PPh}_3)_2$ are present together in solution, only the latter reacts with ethylene at 25°C and 1 atm, as shown by NMR spectra.

By inspection of Figs. 4 and 5 it can be seen that the associative

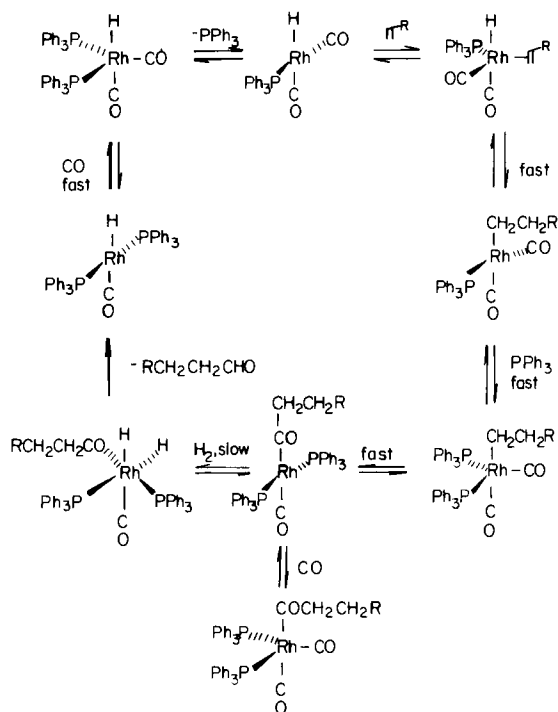


FIG. 4. Dissociative mechanism for the rhodium-triphenylphosphine-catalyzed hydroformylation of olefins (24–27).

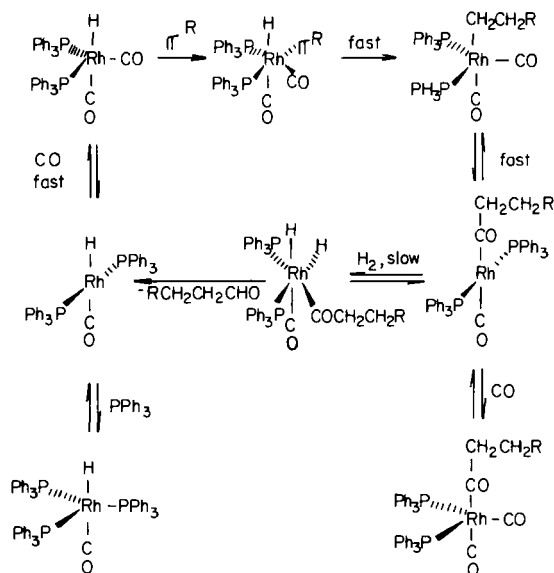


FIG. 5. Associative mechanism for the rhodium-triphenylphosphine-catalyzed hydroformylation of olefins (24-27).

pathway affords more steric hindrance to the coordinating olefin and would be expected to provide preferential formation of the linear alkyl rhodium intermediate. The associative mechanism is preferred at high concentration of catalyst and triphenylphosphine.

IV

SECONDARY PRODUCTS AND REACTIONS

A. Isomer Problems

The principal product of the hydroformylation which is most desired in industrial applications is a linear aldehyde. The unmodified, cobalt-catalyzed processes produce a mixture of linear and branched aldehydes, the latter being mostly an α -methyl isomer. For the largest single application—propylene to butyraldehydes—the product composition has an isomer ratio (ratio of percent linear to percent branched) of (2.5–4.0)/1. The isobutyraldehyde cannot be used to make 2-ethylhexanol, and iso-

butanol has less industrial value than *n*-butanol. Consequently, isomer control of the hydroformylation is of tremendous economic importance and has been the motivating force behind detailed investigations of the mechanism, reaction parameters, and ligand effects.

For unmodified cobalt reactions, the most influential parameter is carbon monoxide partial pressure. This effect is demonstrated in Table II. (See also Section V,A,1.) Hydrogen pressure had a smaller effect (30). Large discrepancies exist in the literature concerning the effect of temperature. At first, temperature was concluded to have a large effect on the product isomer composition (31). Later work (32) showed that the very high reaction rates obtained at high temperatures required vigorous mixing to ensure against depletion of reactant gases in the liquid phase. If depletion occurred, a condition of artificially low P_{CO} resulted and low isomer ratios were obtained. Under conditions of sufficient agitation, temperature had an insignificant effect on isomer ratio.

The relative value of *n*-butyraldehyde and isobutyraldehyde is well exemplified by the recent disclosure (33) of a process for decomposing unwanted isobutyraldehyde back to the elements of propylene, carbon monoxide, and hydrogen for recycling to make more *n*-butyraldehyde.

TABLE II
EFFECT OF CARBON MONOXIDE PARTIAL PRESSURE ON
ISOMERIC DISTRIBUTION OF THE HYDROFORMYLATION
PRODUCTS OF OLEFINS (30)^a

Olefin	P_{CO} (atm)	Isomer ratio
Propylene ^b	2.5	1.6
Propylene ^b	90	4.4
1-Butene ^b	2	1.1
1-Butene ^b	140	3.7
<i>cis</i> -2-Butene ^b	2	1.1
<i>cis</i> -2-Butene ^b	138	2.4
1-Pentene ^c	1.7	1.3
1-Pentene ^c	90	4.5
2-Pentene ^c	1.7	1.3
2-Pentene	93	3.1
4-Methyl-1-pentene ^d	2	1.4
4-Methyl-1-pentene ^d	150	8.1

^a Solvent, benzene or toluene; P_{H_2} , 80 atm; catalyst, $\text{Co}_2(\text{CO})_8$.

^b Temperature 100°C.

^c Temperature 110°C.

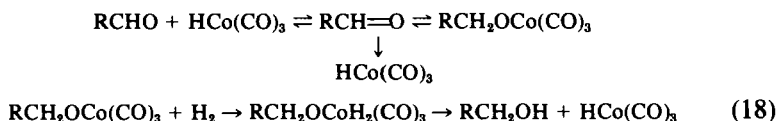
^d Temperature 116°C.

B. Alcohol Formation

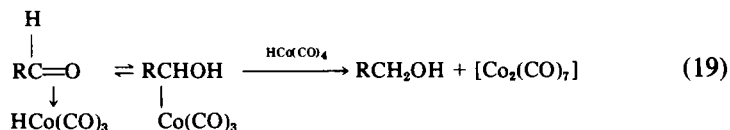
As normally practiced in a cobalt process, the aldehyde product contains about 10% alcohol, formed by subsequent hydrogenation. Marko (34) reported that the hydrogenation is more sensitive to carbon monoxide partial pressure than is the hydroformylation reaction and, in the region between 32 and 210 atm, is inversely proportional to the square of the partial pressure. The full kinetic expression for alcohol formation is expressed by Eq. (17).

$$\frac{d[\text{ROH}]}{dt} = k[\text{R}^1\text{CHO}][\text{Co}][P_{\text{H}_2}][P_{\text{CO}}]^{-2} \quad (17)$$

The key steps in the hydrogenation, as stated by Marko, are given in Eq. (18).



An alternate pathway for the hydrogenation has been suggested by Aldridge and Jonassen (35):



A similar type of intermediate in the ruthenium-catalyzed hydroformylation was suggested by Wilkinson and co-workers (36).

While the 10% of alcohol normally produced during the cobalt hydroformylation is a usable and desired product, the product mixture in the acidic medium forms acetals, and this presents problems in separation and purification. This problem is circumvented if the reaction is modified to produce all alcohols or all aldehydes (Section V,A).

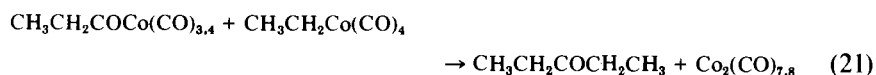
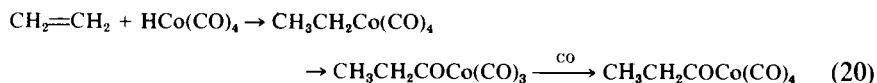
C. Alkane Formation

Interception of the reaction sequence at the alkylcobalt carbonyl stage before "carbonyl insertion," and hydrogenation of this intermediate, produces an alkane. This undesired side reaction is only minor (1-3%) in cobalt-catalyzed hydroformylation of a nonfunctional olefin, but may become predominant with phenyl- or acyl-substituted olefins. Ethylbenzene has been obtained in >50% yield from styrene (37), and even more alkane was obtained from α -methylstyrene (38).

α,β -Unsaturated aldehydes and ketones are mainly hydrogenated to the corresponding saturated compounds (39). In the main, conjugated dienes have yielded practically only monoaldehydes with cobalt catalysts (40).

D. Ketone Formation

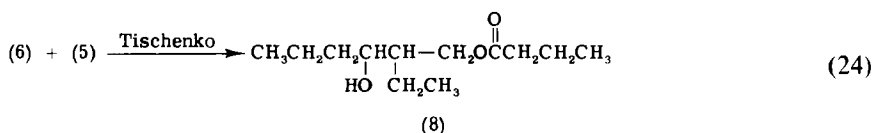
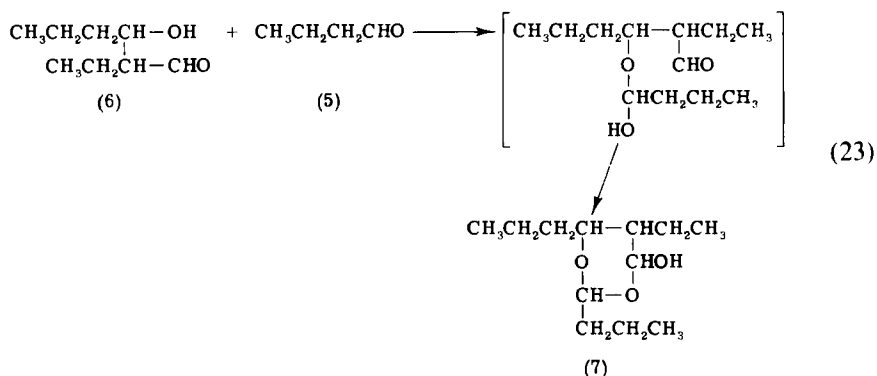
Ketones are formed under conditions of low total pressure and high olefin concentration. Bertrand *et al.* (41) pictured the formation as outlined in Eqs. (20) and (21). Ketone formation is most pronounced with ethylene (least hindered olefin), and diethyl ketone has been obtained in >50% yields (42).



E. Olefin Isomerization

For olefins higher than propylene in chain length, double bond shifts can occur under hydroformylation conditions (30). Isomerization in the cobalt-catalyzed hydroformylation is enhanced by low carbon monoxide partial pressures (<50 atm) and by higher reaction temperatures (150°–190°C) (30). Complete isomerization was observed by Asinger and Berg (43) in the hydroformylation of 1-dodecene at 150°–200°C. The different results obtained by varying the partial pressure of carbon monoxide have been explained by postulating the presence of two catalytic species having different CO/Co ratios, with the one having the lower ratio (more coordinatively unsaturated) being responsible for the isomerization.

Many research groups have attributed the isomerization to a series of additions and eliminations of a cobalt carbonyl hydride. However, it has been shown that aldehydes may be found with formyl groups attached to a carbon atom other than the two of the double bond even under "non-isomerizing" conditions. Piacenti and co-workers (44, 45) studied the hydroformylation of [1-¹⁴C]propylene and of ω -deuterated α -olefins. Even for α -olefins with chain lengths up to C₈, the formyl group was attached to all possible carbon atoms in the product mixture. However, in the deuterated experiments, deuterium was present only on carbons 2, 3, and ω of the resulting aldehydes. These results were explained by pro-



A small amount of formate esters (4%) is formed in the cobalt hydroformylation cycle (46). The amount is undetectable in the rhodium-catalyzed reaction.

V

SUBSTRATES

A. Acyclic Olefins

1. Unmodified Metal Carbonyl Catalysts

The reaction rates of various types of olefins follow much the same pattern with both cobalt- and rhodium-catalyzed systems. Wender and co-workers (47) classified the nonfunctional substrates as straight-chain terminal, internal, branched terminal, branched internal, and cyclic olefins. The results they obtained are given in Table III.

Some significant observations can be made from these results. Straight-chain terminal olefins are the most reactive. Little if any difference exists between 2- and 3-internal, linear olefins. Branching is important only if present at one or more of the olefinic carbon atoms; reaction becomes more difficult as branching increases. Cyclic olefins react in an irregular fashion, but all are less reactive than terminal, linear olefins.

TABLE III
HYDROFORMYLATION OF VARIOUS OLEFINS, COBALT^a (48)

Olefin	Specific rate constant ($10^3 k \text{ min}^{-1}$)
(A) Straight-chain terminal	
1-Pentene	68.3
1-Hexene	66.2
1-Heptene	66.8
1-Octene	65.6
1-Decene	64.4
1-Tetradecene	63.0
(B) Straight-chain internal	
2-Pentene	21.3
2-Hexene	18.1
2-heptene	19.3
3-Heptene	20.0
2-Octene	18.8
(C) Branched terminal	
4-Methyl-1-pentene	64.3
2-Methyl-1-pentene	7.32
2,4,4-Trimethyl-1-pentene	4.79
2,3,3-Trimethyl-1-butene	4.26
Camphene	2.2
(D) Branched internal	
4-Methyl-2-pentene	16.2
2-Methyl-2-pentene	4.87
2,4,4-Trimethyl-2-pentene	2.29
2,3-Dimethyl-2-butene	1.35
2,6-Dimethyl-3-heptene	6.23
(E) Cyclic	
Cyclopentene	22.4
Cyclohexene	5.82
Cycloheptene	25.7
Cyclooctene	10.8
4-Methylcyclohexene	4.7

^a Olefin, 0.5 mole; 65 ml methylcyclohexane; 2.8 g (8.2×10^{-3} mole) $\text{Co}_2(\text{CO})_8$; 110°C ; CO/H_2 1/1; 233 atm. Table reprinted with permission from *J. Am. Chem. Soc.* **78**, 5101 (1956). Copyright by the American Chemical Society.

Similar results were obtained by Heil and Marko (48) for an unmodified rhodium system (see Table IV).

The inclusion of styrene in Table IV is noteworthy. Styrene hydroformylates easily with rhodium catalyst to give a mixture of 2- and 3-phenylpropionaldehyde in good yield (1). This is in contrast to the results reported for the cobalt system, in which hydrogenation to ethylbenzene was the principal reaction.

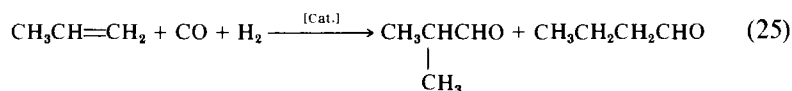
TABLE IV
HYDROFORMYLATION OF VARIOUS OLEFINS,
RHODIUM^a (48)

Olefin	Rate constant (10 ³ k min ⁻¹)
Styrene	124
(A) Linear olefins	
1-Hexene	55.8
1-Octene	50.1
1-Decene	40.5
<i>cis/trans</i> -2-Hexene	34.4
<i>cis</i> -2-Heptene	40.2
<i>cis/trans</i> -3-Heptene	41.9
(B) Branched olefins	
2-Methyl-1-pentene	25.7
2-Methyl-2-pentene	14.7
<i>trans</i> -4-Methyl-2-pentene	29.7
2,4,4-Trimethyl-2-pentene	3.0
2,3-Dimethyl-2-butene	0.7

^a Reaction conditions: 0.5 mole olefin/liter; toluene solvent; 5.3×10^{-2} mmole Rh₄(CO)₁₂/liter; 75°C; 130 atm CO/H₂.

Branching at an olefinic carbon atom inhibited the reaction markedly, the most dramatic case being that of 2,3-dimethyl-2-butene. It should be noted that the product in this case is nearly exclusively 3,4-dimethylpentaldehyde for either cobalt or rhodium catalysis (1). Thus, a general rule that products containing a formyl group attached to a quaternary carbon atom are not formed (49) remains valid. Hydroformylation proceeds only after isomerization has occurred.

Because of the extreme industrial importance of simple hydrocarbons such as propylene in hydroformylation, the reaction of α -olefins has been studied in much detail. As noted before, the formyl group can be attached to either of the carbon atoms which constitute the original double bond. For olefins of greater than C₃ chain length, the formyl group may, under certain conditions, also be attached to a carbon atom which was originally saturated. But for propylene only two isomers are possible, as shown in Eq. (25).



As a result of the desire for obtaining as much of the linear isomer as

possible, both cobalt and rhodium hydroformylations have been studied with product composition as the goal.

For cobalt as catalyst, variations in reaction parameters have been studied as a means of controlling the product composition (or isomer ratio). Thus, variations in isomer ratio from 1:1 to about 4:1 were observed under widely differing conditions of temperature, catalyst concentration, partial pressure of hydrogen, and partial pressure of carbon monoxide.

The most influential parameter in cobalt-catalyzed hydroformylation was found to be carbon monoxide partial pressure. Piacenti *et al.* (30) showed this to be influential for both α - and internal olefins. Results are detailed in Tables V and VI. The percent of *n*-aldehyde rose rapidly as the carbon monoxide partial pressure was increased up to 30–40 atm CO; further increase had little effect. 1-Pentene clearly gave a higher percentage of straight-chain aldehyde than 2-pentene, but the difference was insignificant in the lower P_{CO} experiments.

The hydrogen partial pressure has a small but reproducible effect on the hydroformylation product composition. The direction of the change found was the same as for carbon monoxide partial pressures: the higher P_{H_2} experiments gave higher percentages of *n*-aldehyde.

Conflicting results have been reported for the effects of catalyst concentration in the cobalt-catalyzed reaction. In early work, Hughes and Kirshenbaum (31) reported that these parameters were very influential in determining product composition; high temperatures and high catalyst concentrations resulted in products containing decreased amounts of the

TABLE V
HYDROFORMYLATION OF PROPYLENE AT VARIOUS CO PARTIAL
PRESSURES^a (30)

P_{CO} (atm)	Carbonyl equiv./olefin charged (%)	Straight-chain isomer (%)
2.5	64.0	61.7
6	75.0	65.7
10	84.0	72.6
14	70.0	75.5
21	58.2	79.8
30	50.4	81.1
50	44.5	81.3
90	47.5	81.4

^a Reaction conditions: Propylene, 5 g; $Co_2(CO)_8$, 0.05 g; benzene, 27 g; P_{H_2} , 80 atm; temperature, 80°C.

TABLE VI
HYDROFORMYLATION OF PENTENES AT VARIOUS CO
PARTIAL PRESSURES^a (32)

P_{CO}	A ^b	B	C
1-Pentene			
1.7	55.8	35.6	8.6
2.5	58.2	33.6	8.2
5.5	70.3	25.8	3.9
10	76.8	19.8	3.4
27	80.3	16.8	2.9
50	81.3	15.9	2.8
90	81.7	15.6	2.7
<i>cis- + trans-2-Pentene</i>			
1.7	55.8	35.6	8.6
4.0	66.5	28.1	5.4
5.5	69.3	25.4	5.3
8.5	71.8	23.0	5.2
14	73.8	21.1	5.1
39	75.7	19.2	5.1
45	75.8	19.2	5.0
74	75.8	19.2	5.0
93	75.8	19.2	5.0

^a Reaction conditons: Pentene, 5 g; $\text{Co}_2(\text{CO})_8$, 0.05 g; benzene, 27 g; P_{H_2} , 80 atm; temperature, 80°C.

^b A = % *n*-hexanal of total aldehydes formed; B and C = % 2-methylpentanal and 2-ethylbutanal, respectively.

linear isomer. However, later work suggests that these results may have been artifacts caused by high reaction rates. Both high temperatures and high catalyst concentration increase the rate of aldehyde formation and probably caused a depletion in dissolved carbon monoxide. This would have the same apparent effect as a lower partial pressure of carbon monoxide. Pino *et al.* (32) showed that the rate of agitation, which simulated varying degrees of transport of carbon monoxide from the gas phase to the liquid phase, caused a variation in *n*-hexanal content (from pentene) of 68.5–78.6%. They also found that, provided the reaction rate was controlled by varying the concentration of olefin and of catalyst, the product composition varied only slightly as a function of either temperature or catalyst concentration. Results found are tabulated in Tables VII and VIII.

TABLE VII
EFFECT OF TEMPERATURE ON PRODUCT COMPOSITION IN THE HYDROFORMYLATION OF
PROPYLENE^a (32)

Temperature (°C)	P_{CO} (atm)	g C_3H_6 /100 g solvent	g $Co_2(CO)_8$ /100 g solvent	Straight-chain isomer (%)
80	80	20	1	82.8
90	122	20	1	82.2
100	90	20	1	81.9
110	146	20	1	81.4
120	180	2.5	0.1	81.0
135	170	2.5	0.1	80.5
145	170	2.5	0.1	79.8

^a Benzene solvent; P_{H_2} , 80 atm.

2. Phosphine-Modified Catalysts

The introduction of alkyl phosphine complexes of cobalt carbonyl as hydroformylation catalysts was reported to have a significant effect on product composition (50, 51). Slauch and Mullineaux (52) reported that hexanol with a 91% linear distribution was formed by the hydroformylation of 1-pentene at 150°C, 500 psi, H_2/CO 2.0, catalyst $[Co_2(CO)_8 + 2(n-C_4H_9)_3P]$. Under the same conditions except at a temperature of 190°C, the *n*-hexanol was 84% of the hexyl alcohol produced.

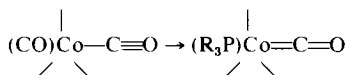
In addition to the increased proportion of linear product, other differences from the unmodified cobalt-catalyzed reaction may be noted. The

TABLE VIII
EFFECT OF CATALYST CONCENTRATION ON PRODUCT
COMPOSITION IN THE HYDROFORMYLATION OF PROPYLENE
CONDUCTED IN THE PRESENCE OF ETHYL ORTHOFORMATE^a
(32)

$Co_2(CO)_8$ (g)	Equiv. carbonyl compd./ mole olefin charged (%)	Linear isomer (%)
0.5	62	73.8
1.0	80	73.9
2.5	83	73.8
2.5	85	73.8
4.0	90	74.1
4.0	82	73.9

^a Reaction conditions: propylene, 20 g; ethanol, 80 g; ethyl orthoformate, 90 g; P_{H_2} , 80 atm; P_{CO} , 230 atm; temperature, 110°C.

pressure of 500 psi is significantly less than that employed in processes using $\text{Co}_2(\text{CO})_8$ [or $\text{HCo}(\text{CO})_4$] as catalyst. Without stabilizing ligands, high partial pressures of carbon monoxide are necessary to maintain the stability of cobalt hydrocarbonyl and prevent decomposition to cobalt metal; the pressure required increases logarithmically as the reaction temperature is increased (53). However, it is recognized that phosphines are stronger σ -donors and poorer π -acceptors than carbon monoxide. Thus, in $\text{Co}_2(\text{CO})_6(\text{PR}_3)_2$ or $\text{HCo}(\text{CO})_3\text{PR}_3$, the remaining carbon monoxide ligands are more strongly bound to the cobalt atom, because the metal tends to transfer the increased electron density back to the ligand.



The substitution of trialkylphosphine for carbon monoxide also makes the metal-hydrogen bond more hydridic in character and results in increased reduction of the initially formed aldehyde to alcohol. Slauch and Mullineaux (52) compared $\text{Co}_2(\text{CO})_8$ and $[\text{Co}_2(\text{CO})_8 + 2\text{PBu}_3]$, each at reaction conditions of 150°C, 500 psi, H_2/CO 1.0, for the hydroformylation of 1-pentene. The products consisted of hexyl aldehydes and hexyl alcohols in the ratios of 95:5 and 30:70, respectively. In a negative aspect of the reaction, they observed 23% hydrogenation of alkene to alkane at a reaction temperature of 195°C with the phosphine-modified catalyst. Tucci (54) reported less alkane formation (4–5%) under more favorable reaction conditions (160°C, H_2/CO 1.2, 1 hour reaction time).

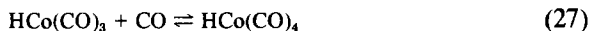
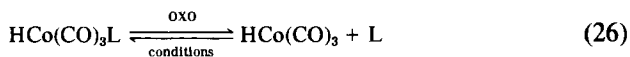
The selectivity to straight-chain product as well as the rate of reaction were found to be greater for the more basic phosphines (52, 55), as shown in Table IX.

These effects of phosphines are explained by observing that the more strongly basic phosphines will dissociate to the least extent in solution (55, 56), Eqs. (26)–(27). The unsubstituted cobalt carbonyl hydride gives

TABLE IX
EFFECT OF PHOSPHINE TYPE ON SPECIFICITY IN THE
HYDROFORMYLATION OF 1-PENTENE (52) OR 1-HEXENE
(55)

L	pK_a Value	Product linearity (%)	
		Ref. (52)	Ref. (55)
$n\text{-Bu}_3\text{P}$	8.4	84.1	89.6
Et_2PhP	6.3	79.0	84.6
EtPh_2P	4.9		71.7
Ph_3P	2.7	66.0	62.4

much greater rates of reaction than the substituted complex; Tucci (57) found a reaction rate ratio of 175 at 120°C. Thus, if an equilibrium exists with small amounts of uncomplexed catalyst being present, the effect of this small amount will be magnified and the rate and product composition will reflect uncomplexed cobalt catalysis.



If ligand dissociation is important, and if it is more extensive when $\text{L} = \text{PPh}_3$ than when $\text{L} = \text{PR}_3$, then the $\text{PPh}_3\text{-Co}$ catalysts system should be very sensitive to changes in ligand concentration. This was found to be the case (55), as shown in Fig. 6.

Another significant and positive characteristic of phosphine-modified cobalt systems is that a high proportion of linear products can be obtained from internal olefins, with only a small sacrifice in reaction rates (58), as shown in Table X.

Tucci (54), studying mainly terminal olefins, cited two reasons for the high selectivity for linear products in the phosphine-modified cobalt catalysts: (a) stereoselective addition of the hydride species to the olefinic double bond, and (b) inhibition of olefin isomerization. However, the results obtained with internal olefins as substrate tended to discount the likelihood of the second reason, and it is generally accepted that selective anti-Markovnikov addition arising from steric hindrance is the principal cause for linear products from nonfunctional olefins.

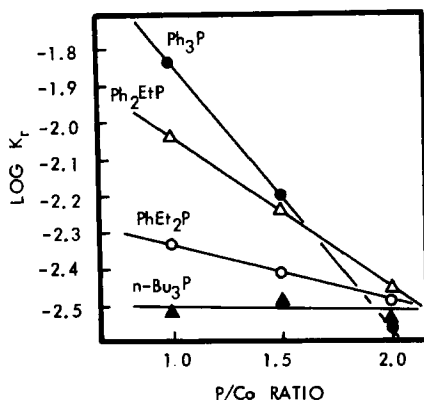


FIG. 6. Concentration effects of various organophosphines on hydroformylation rates. Reprinted with permission from *Ind. Eng. Chem., Prod. Res. Dev.* **9**, 516 (1970). Copyright by the American Chemical Society.

TABLE X
COMPARISON OF HYDROFORMYLATION OF 1-HEXENE AND 2-HEXENE^a (58)

Olefin	Temp (°C)	Alkane (%)	<i>n</i> -ROH (%)	iso-ROH (%)	Selectivity ^b	<i>t</i> _{1/2} (min) ^c
1-Hexene	195	15.2	65.4	16.7	80	100
2-Hexene	195	18.2	65.9	15.5	81	200
1-Hexene	170	14.0	74.8	11.0	87	105
2-Hexene	170	15.2	73.7	11.0	87	90
1-Hexene ^d	170	4.8	67.7	14.7	94	180

^a Reaction of 30.5 ml of olefin in 75 ml of benzene solvent at 400 psi total pressure, $H_2/CO = 2$. Catalyst charge 1.28 g $Co_2(CO)_8$ and 2.56 g Bu_3P . Reaction run overnight (about 17 hours). Table reprinted with permission from *Ind. Eng. Chem., Prod. Res. Dev.* 7, 226 (1968). Copyright by the American Chemical Society.

^b Mol% normal products $\times 100/\text{mol\% normal plus mol\% branched products}$.

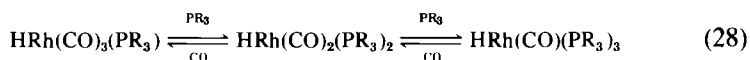
^c Time to consume $\frac{1}{2}$ of the total gas reacted during the run.

^d $H_2/CO = 1$, only 87% conversion of the 1-hexene occurred overnight, also incomplete hydrogenation of the $RCHO$ product to RCH_2OH .

Further progress in providing linear aldehydes from olefinic substrates has been provided by modified rhodium catalysts. Without modifiers, the product from the hydroformylation has very low normal:iso isomer ratios; 1-octene gave only 31% of the linear isomers in one example (28).

In an early investigation (28, 59, 60), critical combinations of several reaction parameters were discovered to produce unusually high yields of the linear isomer. The parameters included low partial pressure of carbon monoxide, high concentration of phosphite or aryl phosphine ligands, and low total gas pressure. The catalyst was a soluble complex of rhodium, formed *in situ* from rhodium metal in many cases. Isomer ratios of 10:1 to 30:1 were obtained by appropriate selection of these reaction parameters. Losses to alkane were minimal, even with P_{CO} as low as 10 psi. Tables XI–XIV illustrate the effects of these various reaction parameters on the product composition.

These effects of the reaction parameters were interpreted in terms of a catalyst equilibrium series, as shown in Eq. (28).



High ligand concentrations and/or low partial pressures of carbon monoxide cause a predominance of species substituted by more than one phosphorus ligand. These species containing multiple ligands present a greater sterically hindered environment for the olefin substrate and favor the linear product (24). Trialkylphosphines, the more basic ligands of the

TABLE XI
HYDROFORMYLATION OF 1-OCTENE AT VARIOUS
TOTAL PRESSURES^a (28)

psi	Reaction time (min)	% Aldehyde which is straight-chain
80-100	50	86
280-300	20	80
560-600	25	74
2500	25	69

^a Octene, 112 g; 5% Rh/C, 15 g; triphenyl phosphite, 15 g; toluene, 200 ml; temperature, 90°C; 1/1 H₂/CO. Table reprinted with permission from *J. Org. Chem.* **34**, 327 (1969). Copyright by the American Chemical Society.

series studied, probably do not participate in multiple substitution because of the increased electron density imposed by the ligand without effective back-bonding ability to remove the density. Likewise, the *o*-substituted triaryl phosphites were less effective. It was concluded that these were too sterically crowded to permit multisubstituted catalyst species.

Wilkinson and co-workers studied in detail the beneficial effects of triarylphosphine modification of rhodium carbonyls (24, 25, 27, 61). In

TABLE XII
HYDROFORMYLATION OF 1-OCTENE WITH VARYING
CONCENTRATIONS OF LIGAND^a (28)

P(OC ₆ H ₅) ₃ (g)	Reaction time (min)	% Aldehyde which is straight-chain
0 ^b	180	31
5.0	30	74
15.0	50	86
30.0	35	87
60.0	65	89

^a Octene, 112 g; 5% Rh/C, 15 g; toluene, 200 ml; temperature, 90°C; 80-100 psi of 1/1 H₂/CO.

^b In the absence of ligand, the reaction would not proceed at the cited conditions of temperature and pressure; slightly more severe conditions were required. Table reprinted with permission from *J. Org. Chem.* **34**, 327 (1969). Copyright by the American Chemical Society.

TABLE XIII
HYDROFORMYLATION OF 1-OCTENE WITH VARIOUS H_2/CO
RATIOS^a (59)

H_2/CO Ratio	Rh/C (g)	Reaction time (min)	% Aldehyde which is straight-chain
1/1	15	30	86
3/1	10	30	90
1/3	10	60	75

^a Octene, 112 g; 5% Rh/C, 10–15 g; toluene, 200 ml; triphenyl phosphite, 15 g; temperature, 90°C; pressure, 80–100 psi.

addition to affording improved isomer ratios, the reaction proceeded under conditions of temperature which were much milder than those effective with cobalt or even phosphine-modified cobalt catalysts. The halide complex $RhCl(CO)(PPh_3)_2$ was effective as a catalyst at temperatures $>60^\circ C$ and pressures of $CO/H_2 > 20$ atm (24). However, with such halide complexes an inhibition period was always observed which could be eliminated by addition of a base such as triethylamine. This suggested that the amine was acting as a hydrogen halide acceptor to form a catalytically active hydride species by hydrogenolysis. The resulting $HRh(CO)(PPh_3)_3$ was highly active as a catalyst, effective even at $25^\circ C$ and 1 atm. From 1-alkenes, approximately 95% of the straight-chain aldehyde was produced.

TABLE XIV
HYDROFORMYLATION OF 1-OCTENE WITH VARIOUS P LIGANDS^a (28)

R in R_3P	Temperature (°C)	Reaction time (min)	% Aldehyde which is straight-chain
<i>n</i> -Butyl	90	225	71
Phenyl	90	35	82
<i>n</i> -Butoxy	110	60	81
Phenoxy	90	50	86
<i>o</i> -Methylphenoxy	90	52	78
<i>o,o</i> -Dimethylphenoxy	90	80	47
<i>p</i> -Phenylphenoxy	90	70	85
<i>p</i> -Chlorophenoxy	90	55	93
<i>p</i> -Methoxyphenoxy	90	270	83

^a Octene, 112 g; toluene, 200 ml; 5% Rh/C, 10 g; R_3P , 0.05 mole; pressure, 80–100 psi 1/1 H_2/CO . Table reprinted with permission from *J. Org. Chem.* **34**, 327 (1969). Copyright by the American Chemical Society.

Information published from several sources about 1970 presented details on both the halide-containing $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ - and the hydride-containing $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ -catalyzed reactions. Brown and Wilkinson (25) reported the relative rates of gas uptake for a number of different olefinic substrates, including both α - and internal olefins. These relative rates are listed in Table XV. 1-Alkenes and nonconjugated dienes such as 1,5-hexadiene reacted rapidly, whereas internal olefins such as 2-pentene or 2-heptene reacted more slowly by a factor of about 25. It should also be noted that substitution on the 2 carbon of 1-alkene (2-methyl-1-pentene) drastically lowered the rate of reaction. Steric considerations are very important in phosphine-modified rhodium catalysis.

In the same study, Brown and Wilkinson reported on the effects of excess phosphine, including an increase in the ratio of straight branched-chain products and also a decrease in the rate of the competing hydrogenation and isomerization reactions. The total rate of reaction was also decreased with excess phosphine, but not to an excessive degree over the range studied. The above conclusions were applicable to 1:1 mixtures of hydrogen and carbon monoxide. A ratio of 2/1 H_2/CO resulted in higher reaction rates and higher isomer ratios, and it also dramatically increased the undesirable hydrogenation and isomerization reactions. Some quantitative data for these trends are given in Table XVI.

Catalytic runs were carried out at higher pressures (400 psi) and tem-

TABLE XV
RELATIVE RATES OF HYDROFORMYLATION OF UNSATURATED
COMPOUNDS^a (25)

Substrate	Rate ^b	Substrate	Rate ^b
Allyl alcohol	7.05	1-Heptene	3.50
Allyl phenyl ether	5.78	1-Dodecene	3.18
Styrene	4.32	Vinyl acetate	0.75
1,5-Hexadiene	4.26	Cyclooctene	0.26
4-Vinylcyclohexene	4.21	Ethyl vinyl ether	0.20
<i>o</i> -Allylphenol	4.03	2-Pentenenes	0.15
1-Pentene	3.74	<i>cis</i> -2-Heptene	0.12
Allyl cyanide	3.72	<i>dl</i> -Limonene	0.10
Allyl benzene	3.56	2-Methyl-1-pentene	0.06
1-Hexene	3.52		

^a Catalyst, $\text{HRh}(\text{CO})(\text{PPh}_3)_3$, 2.5 mm; solvent, benzene, olefin concentration 1.0 M; temperature, 25°C; pressure, 500 mm of 1/1 H_2/CO . Table reprinted with permission from *J. Chem. Soc. A*, p. 2753 (1970). Copyright by the Chemical Society.

^b Rate measured as gas uptake in ml min^{-1} . 1:1:1 Mixtures of alkene, hydrogen, and carbon monoxide at 600 mm total pressure gave uptakes for ethylene and propylene of 4.55 and 1.60 ml min^{-1} , respectively.

TABLE XVI
REACTION PRODUCTS FROM THE HYDROFORMYLATION OF 1-HEXENE^a (25)

Moles excess PPh ₃	Temperature (°C)	H ₂ /CO	<i>n</i> -Aldehyde (% of total)	Hydrogenation and isomerization products (%)
0	25	1	86	< 4
0	40	1	88	< 4
3	25	1	92	< 4
3	40	1	93	<i>ca</i> 4
0	25	1.25	91	10
0	40	1.25	95	22
0	40	2.0	97	60
3	40	2.0	98.5	31

^a HRh(CO)(PPh₃)₃, 30 mM; benzene solvent; substrate concentration, 1 M; 1 atm H₂/CO.

peratures of 25°, 45°, and 65°C, with no excess phosphine, and a gas ratio of 1/1 H₂/CO. Low isomer ratios of (2–4): 1 were obtained. When the gas ratio was 2/1, the isomer ratio was still low and the competing hydrogenation and isomerization reactions were serious. However, conducting the reaction with a 100-fold molar excess of triphenylphosphine gave a slightly higher isomer ratio (5.6) and decreased the competing reactions to a combined 4–5%. In an “ultimate” reaction conducted in molten triphenylphosphine under 400 psi, high rates were obtained, as well as isomer ratios up to 16: 1, but the competing hydrogenation accounted for 7–25% of the product composition.

Another study in 1970 (62) reported a HRh(CO)(PPh₃)₃-catalyzed reaction at 500 psi and 107°C. It was found that as a general rule, propylene gave an isomer ratio of about 2: 1, whereas higher α -olefins gave ratios of about 3: 1. Under these general conditions conversions and selectivities to aldehyde were excellent, as noted in Table XVII [see also (63)].

The rate of hydroformylation was found to vary in a nonlinear fashion as a function of triphenylphosphine concentration. A maximum in rate was noted at a triphenylphosphine/HRh(CO)(PPh₃)₃ weight ratio of (5–10): 1, as illustrated in Fig. 7. A maximum in selectivity to linear aldehyde was noted at about a 5: 1 ratio, and no significant further increase was noted up to a 50: 1 ratio of triphenylphosphine to rhodium complex.

In these studies it was also reported that butyraldehyde isomer ratios were increased by lowering the partial pressure of carbon monoxide, but that this decrease in P_{CO} caused a dramatic and parallel increase in propane formation. It was concluded that propane was formed in lieu of isobutyraldehyde at low P_{CO} . This effect is illustrated in Fig. 8.

Craddock *et al.* (64) studied the hydroformylation of α -olefins (princi-

TABLE XVII
 HYDROFORMYLATION OF HIGHER OLEFINS^a (62)

Olefin feed	H ₂ /CO	Linear isomer (%)	Selectivity to aldehyde (%)
1-Octene	1.9	72	97
C ₇ -C ₉ ^b	3.0	67	97
C ₁₄ -C ₁₆ ^c	4.0	71	97

^a Solvent, product aldehyde; pressure, 500 psi; temperature, 107°C; catalyst, 3/1 weight ratio of PPh₃ to HRh(CO)(PPh₃)₃.

^b Chevron cracked-wax α -olefin.

^c Gulf α -olefin from ethylene polymerization.

pally 1-hexene) catalyzed by the halide catalyst RhCl(CO)(PPh₃)₂ under 500–1000 psi total reaction pressure and temperatures of 100°–150°C. Excess triphenylphosphine ligand levels of 0 to >50 triphenylphosphine molecules per rhodium atom were also included in the study. Excess ligand increased the percentage of linear aldehyde, as shown in Table XVIII.

Experiments with internal olefins demonstrated that isomerization is very rapid at temperatures at or above 150°C with no excess ligand, and is rapid in the presence of excess phosphines if the temperature is 200°C or above (Table XIX).

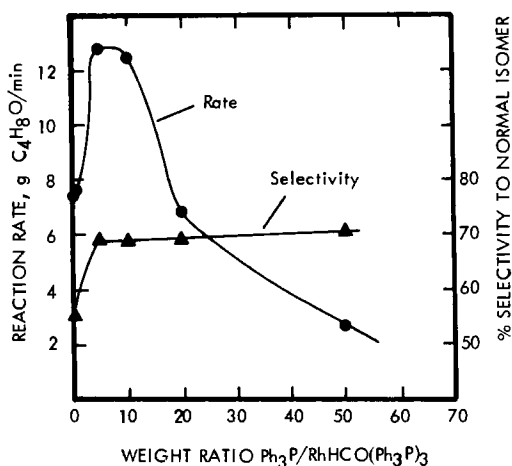


FIG. 7. Effect of triphenylphosphine concentration on rate and selectivity. Reprinted with permission from *Hydrocarbon Process.* p. 112 (April, 1970). Copyright by Gulf Publishing Company.

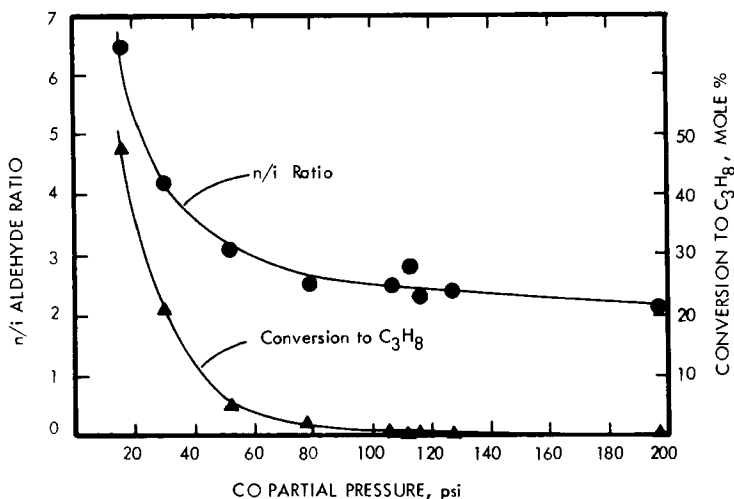


FIG. 8. Effect of the partial pressure of carbon monoxide on normal to isoaldehyde ratio and conversion to propane. Reprinted with permission from *Hydrocarbon Process.* p. 112 (1970). Copyright by Gulf Publishing Company.

Solvents were shown to have a marked effect upon the rate of reaction and in some cases to alter the product distribution. Without excess triphenylphosphine, as the polarity and concomitant basicity of the solvent increased, the selectivity of the catalyst also increased. Addition of excess triphenylphosphine to the polar solvent dimethylformamide resulted in a further increase in selectivity as well as a fourfold acceleration in rate. Results obtained in various types of solvents are summarized in Table XX.

Another pertinent observation is the fact that the reaction proceeded twice as fast in *n*-butyraldehyde (polar) as in benzene (nonpolar), even though the catalyst concentration was reduced to only one-third the comparable level. A graphic illustration of this effect is given in Fig. 9. The rate of gas uptake is plotted as a function of time for a reaction conducted in benzene and again for a second reaction conducted in butyraldehyde. The rate of reaction in the polar solvent was initially fast and decreased with time. The rate in the nonpolar benzene was initially slow, became faster as the solvent became more polar with the presence of product aldehyde, and then subsequently diminished with time. When the data were replotted as the log of unreacted olefin vs. time, the polar medium reaction showed first-order dependence on olefin concentration, whereas the nonpolar solvent reaction showed no definite order, owing to the constantly changing polarity.

Branching in the olefinic structure at one or both of the double-bonded

TABLE XVIII
EFFECT OF EXCESS LIGAND UPON PRODUCT DISTRIBUTION^a (64)

[PPh ₃]"excess" (M)	Ratio PPh ₃ /Rh	Product distribution (mol%)					Selectivity ^d
		Hexane	Hexene	1-Heptanal	2MH ^b	2EP ^c	
0	0	0.3	3.0	40.6	40.9	15.2	42.0
3.3×10^{-3}	5	—	3.9	64.0	32.1	—	66.7
1.3×10^{-2}	20	—	4.8	72.5	22.7	—	76.2
3.2×10^{-2}	50	Trace	4.6	72.5	22.6	0.3	76.2

^a RhCl(CO)(PPh₃)₂, 6.7×10^{-4} M; pressure, 500 psi 1/1 H₂/CO; temperature, 100°C; reaction time, 17 hours; solvent, 50 ml benzene; olefin, 25 ml 1-hexene. Table reprinted with permission from *Ind. Eng. Chem., Prod. Res. Dev.* **8**, 291 (1969). Copyright by the American Chemical Society.

^b 2-Methylhexanal.

^c 2-Ethylpentanal.

^d Percent of total aldehyde which is 1-heptanal.

TABLE XIX
EFFECT OF EXCESS LIGAND UPON PRODUCT DISTRIBUTION FROM INTERNAL OLEFIN^a
(64)

Olefin	[PPh ₃]' ^b excess'' (M)	Temp. (°C)	Isomer distribution in product			Olefin conversion (%)
			1-Heptanal	2MH ^b	2EP ^c	
2-Hexene	0	150	36.8	45.5	17.7	99.3
2,3-Hexene mix	0	150	35.3	45.7	19.0	93.9
1-Hexene	0	150	40.1	41.9	18.0	99.5
2-Hexene	0	200	38.5	45.1	16.4	34.1
2-Hexene	7×10^{-2}	150	16.1	55.8	28.1	99.4
2-Hexene	7×10^{-2}	200	43.0	41.4	15.6	79.3

^a RhCl(CO)(PPh₃)₂, 1.3×10^{-3} M; pressure, 500 psi 1/1 H₂/CO; reaction time, 17 hours; solvent, 75 ml dioctyl phthalate; olefin, 25 ml. Table reprinted with permission from *Ind. Eng. Chem., Prod. Res. Dev.* **8**, 291 (1969). Copyright by the American Chemical Society.

^b 2-Methylhexanal.

^c 2-Ethylpentanal.

carbon atoms affects both the rate of reaction and the product distribution. 2-Methyl-1-pentene reacts at about half the rate of 1-hexene (48), 2,3-dimethylbutene at one-eightieth the rate. In addition, the product from the latter obtained by reaction at 140°C, 160 atm of H₂/CO, and Rh₂O₃ as catalyst consisted almost entirely of 3,4-dimethylpentanol (65).

TABLE XX
EFFECT OF SOLVENTS (64)

Solvent	[Rh] (M)	[PPh ₃] (M)	<i>t</i> _{1/2} (min)	Isomer distribution (mole %)		
				1-Heptanal	2MH ^a	2EP ^b
Benzene	6.7×10^{-4}	0	157	41.9	42.3	15.8
DMF	6.7×10^{-4}	0	132	70.9	28.8	0.3
DMF	6.7×10^{-4}	2.7×10^{-1}	35	74.4	25.6	Trace
Diphenyl ether	6.7×10^{-4}	2.7×10^{-1}	212	74.9	25.1	Trace
Benzene	1.3×10^{-3}	4.5×10^{-2}	90	74.0	26.0	—
<i>n</i> -Butyraldehyde	4.5×10^{-3}	4.5×10^{-2}	45	73.0	27.0	—
Dioctyl phthalate	1.3×10^{-3}	0	130	52.1	35.5	12.4
Dioctyl phthalate	1.3×10^{-3}	4.5×10^{-2}	112	72.5	27.1	0.4

^a 2-Methylhexanal. Table reprinted with permission from *Ind. Eng. Chem., Prod. Res. Dev.* **8**, 291 (1969). Copyright by the American Chemical Society.

^b 2-Ethylpentanal.

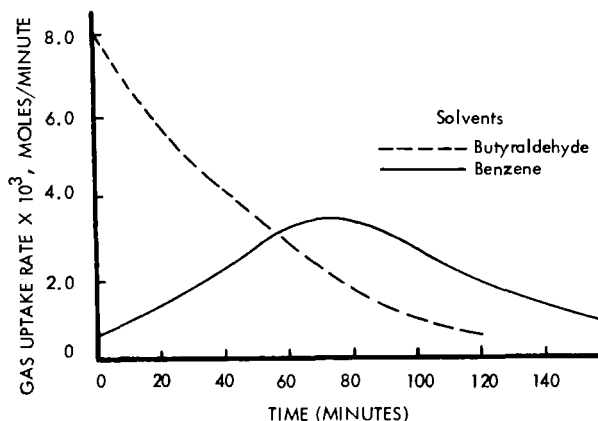


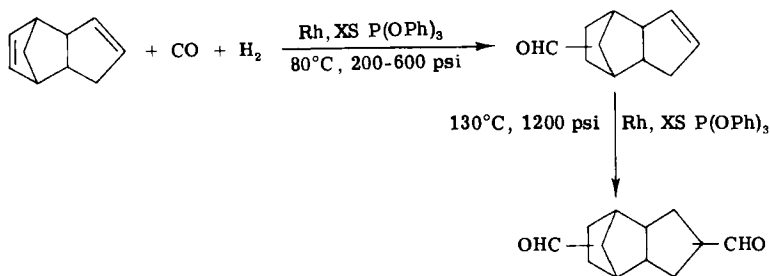
FIG. 9. Effect of solvent variation on hydroformylation of 1-hexene. Reprinted with permission from *Ind. Eng. Chem., Prod. Res. Dev.* **8**, 291 (1969). Copyright by the American Chemical Society.

Thus, the rule of Keulemans (49), that α -quaternary carbon formyl compounds are not formed, was followed. The olefin isomerized to allow formyl attachment to a primary carbon atom. Addition of phosphine, which decreases isomerization, resulted in no reaction.

B. Cyclic Olefins

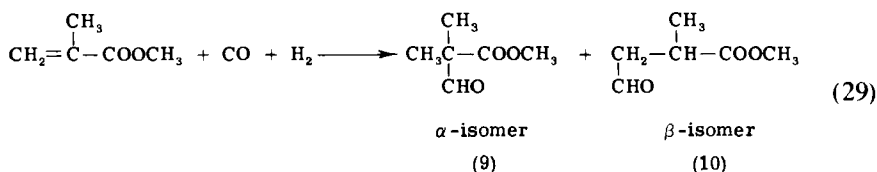
Differences in reactivity have been exhibited between acyclic and different types of cyclic olefins. Vinylcyclohexene in a cobalt hydroformylation at 120°–134°C and 475–720 atm pressure gave a 65% yield of a mixture of mono- and dialdehydes (66).

Dicyclopentadiene has produced some interesting results. With rhodium catalyst at 115°C in tetrahydrofuran (THF), the dialdehyde was produced in good yield; at 180°C that reaction proceeds further to form the diol in 67% yield (67). With a rhodium catalyst modified by excess triphenyl phosphite, the unsaturated monoaldehyde was obtained in a rapid reaction under very mild conditions (68, 69). The nonstrained 5-membered ring olefin required more strenuous conditions for hydroformylation. Either compound could be obtained in good yield by proper choice of conditions.



C. α,β -Unsaturated Aldehydes, Ketones, and Esters

α,β -Unsaturated aldehydes and ketones are mainly hydrogenated to the corresponding saturated compound (39). However, α,β -unsaturated esters may be hydroformylated smoothly. Acrylates and methacrylates have been the subject of considerable investigation. These substrates respond most dramatically to variations in reaction conditions with cobalt and with rhodium catalysis; both α - and β -isomers may be obtained in very high specificity.



One of the most interesting observations is that the α -isomer (9) contains a quaternary carbon atom attached to the formyl group, which is a violation of the rule of Keulemans (49). It must be that electronic effects are dominant for this type of substrate, particularly when the effects of phosphine-modified rhodium systems are considered (*vide infra*).

Falbe and Huppel (70) reported that the cobalt hydroformylation of ethyl acrylate at 300 atm and 140°C gave >90% yield of the β -isomer (10), which was hydrogenated at temperatures of 200°–250°C. The final product was a lactone, as shown in Eq. (30).

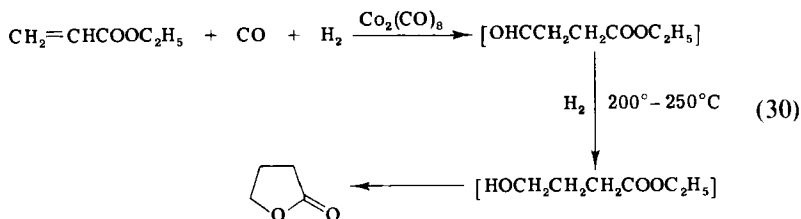


TABLE XXI
HYDROFORMYLATION OF METHYL METHACRYLATE AT VARIOUS
PRESSURES^a (70)

Aldehyde isomer	200 atm	400 atm	500 atm	1000 atm
α (9)	42%	48%	52%	72%
β (10)	42%	42%	31%	13%

^a Solvent, benzene, 4 \times substrate; catalyst, Rh₂O₃, 0.04 mol%; temperature, 80°C.

The products of the rhodium-catalyzed hydroformylation were responsive to the reaction temperatures and, to a lesser degree, to the reaction pressure, as shown in Tables XXI–XXII.

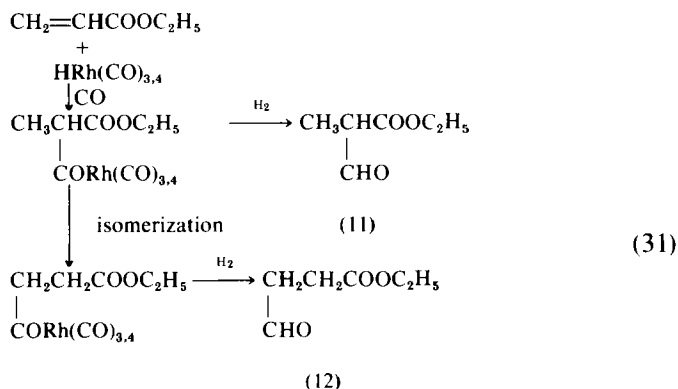
Catalysis by rhodium-tri-*n*-butylphosphine resulted in high yields of product containing a marked predominance of the α -isomer, which is contrary to the trend expected from a steric point of view. Again, high pressure favored the α -isomer, and 400 atm resulted in a 91% yield of this product.

The results with α,β -unsaturated esters, and in particular the effects of temperature and pressure of hydrogen and of carbon monoxide, have been interpreted (71) in terms of an intermediate alkylrhodium carbonyl, as outlined in Eq. (31). The branched-chain alkylrhodium carbonyl was pictured as being formed first. This could then be hydrogenated immediately to the α -isomer (11), or isomerized and then hydrogenated to the β -isomer (12). Higher temperatures promote the isomerization and cause the percentage of α -carboethoxypropionaldehyde to decrease. Higher pressures of carbon monoxide inhibit the isomerization and result in increased percentages of the α -isomer. High pressures of hydrogen favor the hydrogenation and would thus tend to promote hydrogenation of the initially formed branched-chain intermediate before isomerization could occur.

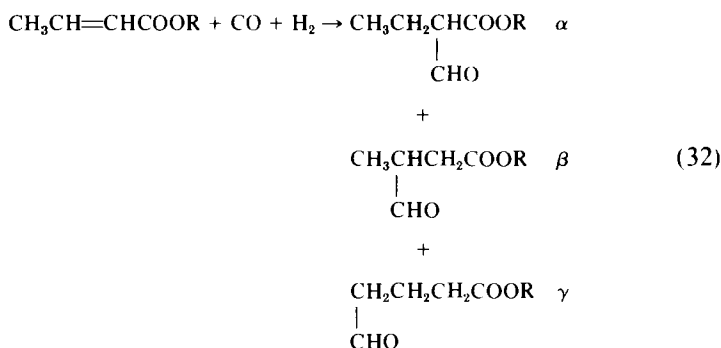
TABLE XXII
HYDROFORMYLATION OF METHYL METHACRYLATE AT
VARIOUS TEMPERATURES^a (70)

Aldehyde isomer	80°C	100°C	120°C	150°C
α (9)	72%	54%	35%	11%
β (10)	13%	30%	50%	71%

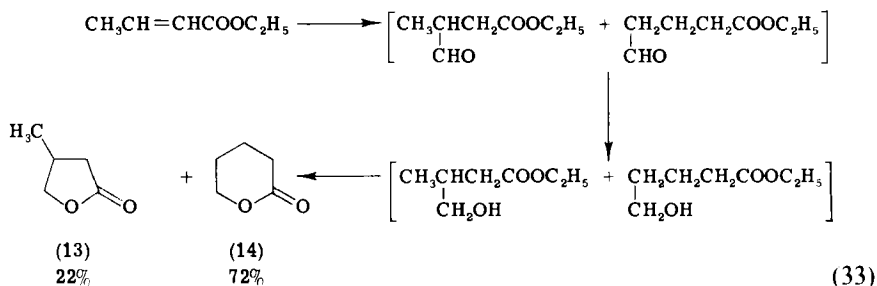
^a Solvent, benzene; catalyst, Rh₂O₃, 0.04 mol%; pressure, 1000 atm 1/1 H₂/CO.



In the hydroformylation of crotonate esters, three different aldehydes may be formed, denoted as the α -, β -, or γ -isomers:



The cobalt-catalyzed reaction was studied by isolation of the lactones formed by hydrogenation and lactonization at higher temperatures (73). The hydroformylation was conducted at 140°C and 300 atm, followed by hydrogenation and cyclization at 200°–240°C, Eq. (33).



With rhodium catalysts, higher amounts of the lactone which is formed

TABLE XXIII
HYDROFORMYLATION OF ETHYL CROTONATE
WITH SUBSEQUENT HYDROGENATION^a (70)

Temperature (°C) ^b	Yield (%)			
	α^c	β^d	δ^e	Total ^f
70-90	21	15	1	55
100-110	9	32	1	60
120	6	46	3	74
130	5	52	5	81
135	3	60	9	92
140	2	55	11	88
150	1	43	15	79
180	—	31	30	91 ^g

^a Catalyst, Rh₂O₃, 1 wt %; pressure (hydroformylation), 200 atm; (hydrogenation), 300 atm; temperature of hydrogenation, 230°C.

^b Temperature of the hydrogenation reaction.

^c Ethyl α -hydroxymethyl butyrate.

^d β -Methylbutyrolactone.

^e δ -Valerolactone.

^f Ethyl butyrate 17-20%.

^g Ethyl butyrate 30% in this example.

TABLE XXIV
HYDROFORMYLATION OF (X)^a-HEXENOIC ACID METHYL ESTERS^b (73)

X ^a	Temperature (°C)	Catalyst	Composition of product (%) ^c				
			I	II	III	IV	V
3	120	Rh ₂ O ₃	1	36	28	28	8
3	160	Rh ₂ O ₃ + PR ₃ ^d	—	66	34	—	—
3	120	Rh ₂ O ₃ + PR ₃ ^e	1	66	32	1	—
5	120	Rh ₂ O ₃	Trace	3	12	41	44
5	160	Rh ₂ O ₃ + PR ₃ ^d	—	—	—	39	61

^a X = 3, CH₃CH₂CH=CHCH₂COOCH₃; X = 5, CH₂=CHCH₂CH₂CH₂COOCH₃.

^b Catalyst, Rh₂O₃, 0.24 mol% (0.2 g); PR₃, 7.7 mol% (P/Rh = 30); substrate, 0.33 mole; pressure, 200 atm 1/1 H₂/CO; solvent, benzene, 200 ml.

^c total yield > 90%. Roman numerals refer to position of carbon relative to the ester group, to which the formyl group is attached. I = α , II = β , etc.

^d Tri-*n*-butylphosphine.

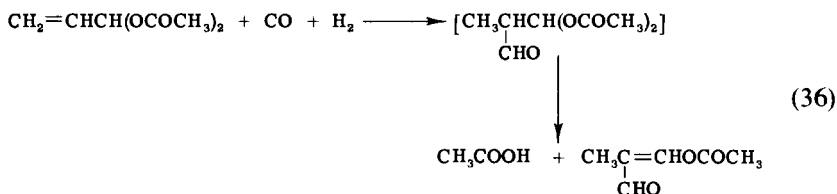
^e Tricyclohexylphosphine.

TABLE XXV
 HYDROFORMYLATION OF ETHYL CINNAMATE (70)

Catalyst (mol%)	Temperature (°C)	Pressure (atm)	Time	Yield (%)	
				15 ^a	16 ^b
Co ₂ (CO) ₈ (5)	250	300	5	8.5	91.5
Rh ₂ O ₃ (0.07)	(1)120	200	4		
	(2)230	300	5.5	73.0	26.0

^a β -Phenyl- γ -butyrolactone.^b Ethyl hydrocinnamate.

initially formed compounds underwent further hydrogenolysis and condensation reactions. Rhodium oxide also catalyzed the hydroformylation of the diethyl acetal at 100°C and 200 atm. The products were the *n*- and isoaldehyde formed in a 1:2 ratio, respectively. However, when the diacetate of acrolein was the substrate and benzene the solvent, rhodium catalysis resulted in the formation of 2-methyl-3-acetoxyacrolein and acetic acid as the only isolable products:

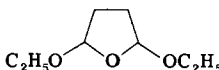
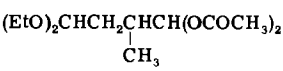
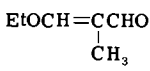


The cobalt-catalyzed hydroformylation of acrolein diacetate in ethanol proceeded in a complicated fashion. The products obtained are listed in Table XXVI. These products are rationalized by the following sequence: The initial products formed were *n*-aldehyde (1,1-diacetoxy-3-formylpropane, ca. 60%), isoaldehyde (1,1-diacetoxy-2-formylpropane, 5–10%) and propionaldehyde diacetate, ca. 5%. In the alcohol solvent, the aldehydes were converted to the corresponding acetals. A portion of the *n*-aldehyde was converted to 2,5-diethoxytetrahydrofuran by acid catalysis, and the isoaldehyde was thermally decomposed to 2-methyl-3-acetoxyacrolein.

Finally, cobalt hydroformylation of acrolein diacetate in ethanol, in the presence of excess ethyl orthoformate, simplified the reaction and resulted in high yields of 1,1-diacetoxy-4,4-diethoxybutane (*n*-isomer), lower yields of 1,1-diacetoxy-2-methyl-3,3-diethoxypropane (iso). The favorable effects of ethyl orthoformate are shown in Table XXVII.

An effect of substitution on one of the carbon atoms of the double bond was again demonstrated by the rhodium-catalyzed hydroformyla-

TABLE XXVI
HYDROFORMYLATION OF ACROLEIN DIACETATE (74)

Reaction product	Yield (%)
$\text{OHCCH}_2\text{CH}_2\text{CH(OCOCH}_3)_2$	2.0
$(\text{EtO})_2\text{CHCH}_2\text{CH}_2\text{CH(OCOCH}_3)_2$	45.5
	10.3
	0.8
	5-10
$\text{CH}_3\text{CH}_2\text{CH(OCOCH}_3)_2$	4.9

tion of α -alkylacrolein diacetals (75). The reaction at 80°C and 100 atm of H_2/CO , with $\text{RhCl(CO)(PPh}_3)_2 + (\text{C}_2\text{H}_5)_3\text{N}$ as catalyst, of diethyl acetals gave high yields of the more linear product.

The hydroformylation of acrolein cyclic acetals has received considerable attention in the recent patent literature as a route to 1,4-butanediol (76-82). This diol is a comonomer for the production of polybutylene terephthalate, an engineering thermoplastic. The standard method for its manufacture has been from acetylene and formaldehyde, as shown in Eqs. (37) and (38):



TABLE XXVII
HYDROFORMYLATION OF ACROLEIN DIACETATE IN THE
PRESENCE OF ETHYL ORTHOFORMATE (74)

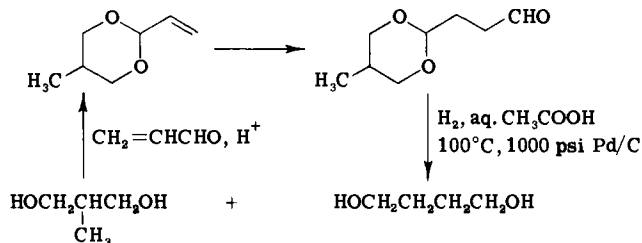
Ratio EO/EA ^a	<i>n</i> -Isomer (% yield)	Iso (% yield)
0	36.5	—
0.5	56.9	1.3
1.0	69.7	2.0
1.0	74.2	2.9
1.2	76.0	2.7
1.4	78.6	3.0
1.5	80.0	3.9

^a Mole ratio of ethyl orthoformate to acrolein diacetate.

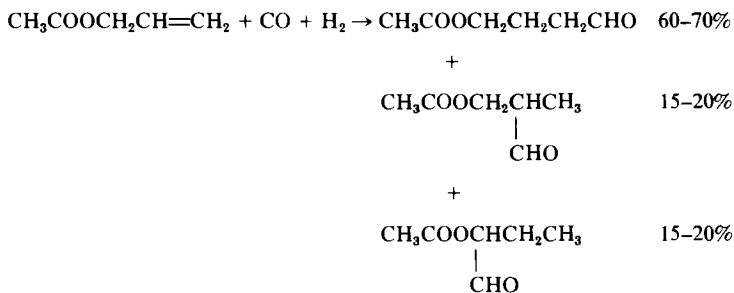
Acrolein is manufactured from low-cost propylene, and its hydroformylation to 1,4-butanediol or a precursor of it could provide a more economical route.

Both modified cobalt and modified rhodium systems have been successfully employed. In general, both have produced good yields of linear aldehyde. Results are tabulated in Table XXVIII.

The product aldehyde was converted to butanediol by hydrolysis and hydrogenation.



Another route to the diol monomer is provided by hydroformylation of allyl alcohol or allyl acetate. Allyl acetate can be produced easily by the palladium-catalyzed oxidation of propylene in the presence of acetic acid in a process similar to commercial vinyl acetate production. Both cobalt- and rhodium-catalyzed hydroformylations have received much attention in recent patent literature (83–86). Hydroformylation with cobalt carbonyl at 140°C and 180–200 atm H_2/CO (83) gave a mixture of three aldehydes in 85–99% total yield.

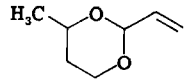
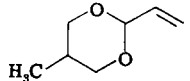
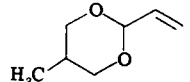
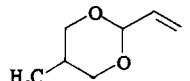


Hydrolysis and hydrogenation gave 1,4-butanediol.

It has been reported (86) that these same three isomeric aldehydes were formed from allyl acetate by a reaction catalyzed by rhodium trichloride and iron pentacarbonyl. Reaction proceeded at 135°C under 300 atm of H_2/CO , but the product composition was not specified.

Allyl alcohol may be a preferred olefin for rhodium hydroformylation routes to 1,4-butanediol. Comparison of allyl acetate and allyl alcohol as

TABLE XXVIII
HYDROFORMYLATION OF ACRYLEIN CYCLIC ACETALS

Substrate	Catalyst	Modifier ^a	Temp. (°C)	Pressure (psi)	Yield ^b	% <i>n</i> ^b	% Iso ^b	Ref.
	Rh ₆ (CO) ₁₆	Rh ₃ P	86	90	—	> 85	< 15	77,78
	Rh ₆ (CO) ₁₆	(CH ₃ O) ₃ P	110	105	97	80	12	79–81
	HRh(CO)(PPh ₃) ₃	Ph ₃ P	140	300–600	89	68	32	82
	Co ₂ (CO) ₈	(C ₆ H ₁₇) ₃ P	150	1000–1200	86 ^c	81	19	

^a All phosphine ligands were in molar excess over Rh.

^b Yield of product aldehyde, % *n* and % iso of the aldehyde product.

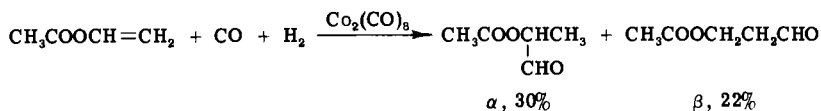
^c Composed of 67% aldehyde, 19% alcohol.

substrates with both rhodium and cobalt catalysts have been made (87); the results are given in Table XXIX.

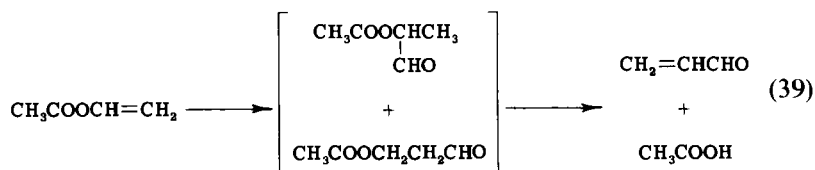
Similar results with allyl alcohol were obtained by Kawahito and Ikeda (88). A rhodium tributylphosphine system gave 66% 1,4-butanediol and 22% 2-methyl-1,3-propanediol.

D. Unsaturated Ethers and Alkenyl Esters

Early studies of the cobalt hydroformylation (4) included vinyl acetate as the olefinic reactant. A mixture of α - and β -formyl esters was reported.



Essentially the same results were obtained in a later study (89). The maximum yields were obtained at 160°C; the competing reaction was a decomposition of the initially formed aldehyde:



The percentage of linear aldehyde increased with increasing reaction

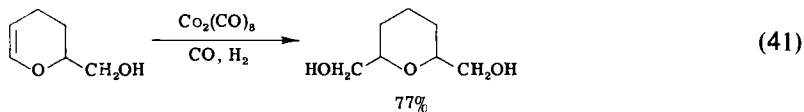
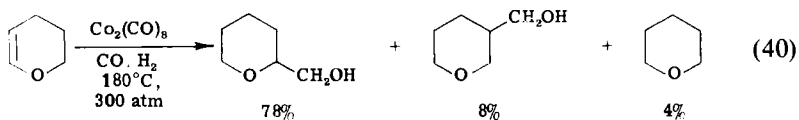
TABLE XXIX
HYDROFORMYLATION OF ALLYL ACETATE AND ALLYL ALCOHOL

Substrate	Catalyst	Conditions	Products, yield
Allyl alcohol	HRh(CO)(PPh ₃) ₃ + PPh ₃	30°C, 20 psi 1/1 H ₂ /CO	57% 1,4-Butadiene ^a 35% 2-Methyl-1,3-propanediol ^a
Allyl alcohol	HRh(CO)(PPh ₃) ₃ + PPh ₃	30°C, 20 psi 4/1 H ₂ /CO	77% 1,4-Butanediol ^a 19.5% 2-Methyl-1,3-propanediol ^a
Allyl acetate	HRh(CO)(PPh ₃) ₃ + PPh ₃	30°C, 20 psi 1/1 H ₂ /CO	No reaction
Allyl acetate	HRh(CO)(PPh ₃) ₃	120°C, 1800 psi 1/1 H ₂ /CO	45% 4-Acetoxybutyraldehyde 48% 2-Methylpropionaldehyde
Allyl acetate	Co ₂ (CO) ₈	120°C, 1800 psi 1/1 H ₂ /CO	52.6% 4-Acetoxybutyraldehyde Seven other products

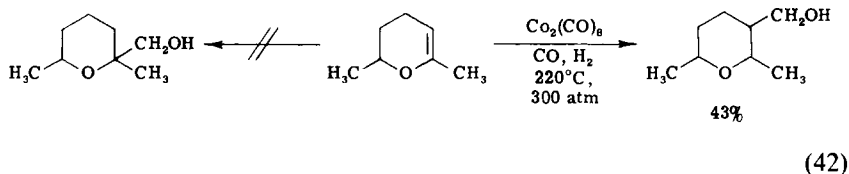
^a After hydrogenation.

Fell and Barl (89) also studied the rhodium-catalyzed reaction. A rhodium-*N*-methylpyrrolidine-water catalyst system was very effective for producing the propane-1,2-diol acetate directly. The best yields (>90%) of product of about 9:1 alcohol:aldehyde ratio were obtained in the region of 95°–110°C. This range was very critical, as were other reaction parameters. Rhodium alone gave the best yield of *aldehyde* (83%) at 60°C. Triphenylphosphine as cocatalyst induced the decomposition of the aldehyde product.

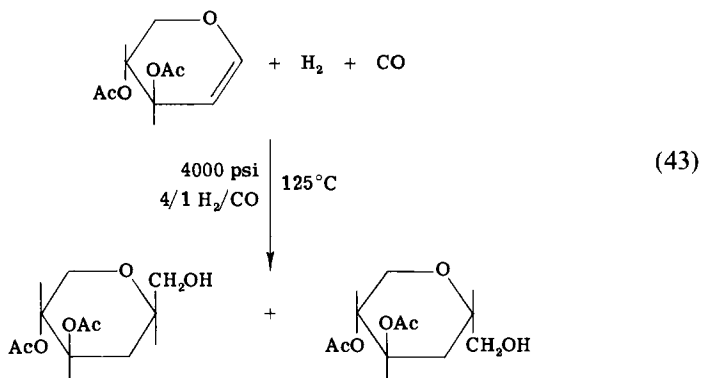
Falbe and Korte (90) studied the cobalt hydroformylation of dihydropyran and its derivatives. The reactions were conducted at temperatures above 180°C, with pressures of 300 atm of 1/1 H₂/CO. Under these conditions, the initially formed aldehydes were hydrogenated to the alcohols *in situ*. As noted with acyclic vinyl ethers, formyl attachment was predominantly α .



Substitution on the double-bond carbon α to the oxygen increased the difficulty of the reaction, and formyl attachment occurred exclusively on the β -carbon [Eq. (42)]. Thus, these substituted olefins also followed the rule of Keulemans (49).



Rosenthal and co-workers (91, 92) studied the cobalt hydroformylation of various unsaturated carbohydrates. As with other α,β -unsaturated ethers, addition of the formyl group occurred almost exclusively at the double-bond carbon α to the oxygen. High yields of product were obtained, but hydrogenation to alcohol was facile, even under mild conditions, as noted in Eq. (43):

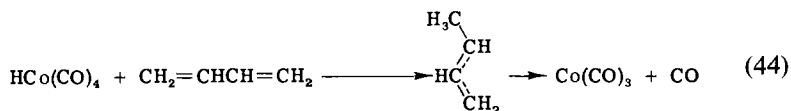


By careful control of reaction conditions, modest yields of the intermediate aldehyde could be obtained.

E. Conjugated Dienes

1,3-Butadiene, the simplest conjugated diene, appears to be a promising substrate for the hydroformylation reaction, because the expected product (hexanedial) could be easily converted to useful products. Oxidation would produce adipic acid, hydrogenation hexanediol, and reductive amination hexamethylenediamine. However, this objective has been difficult to realize.

Cobalt hydroformylation of butadiene produced low yields (24%) of an equimolar mixture of *n*- and isovaleraldehyde (40). It has been established that the cobalt hydrocarbonyl adds to form a stable π -allyl complex (93, 94).

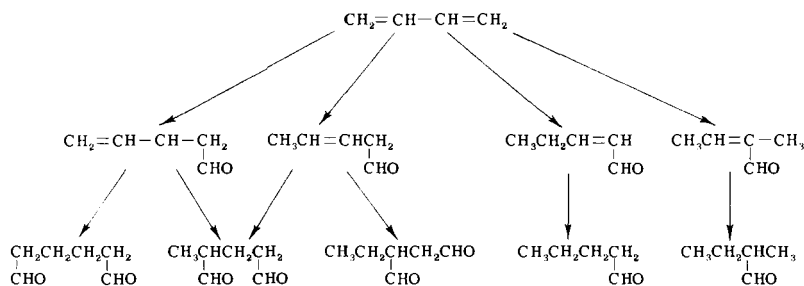


This complex then reacts with H_2/CO to give a monoaldehyde.

Fell and Rupilius (95) found that a rhodium tributylphosphine catalyst

was effective for the partial bishydroformylation of butadiene. The hydroformylation was carried out at 125°C under 200 atm of 2/1 H₂/CO pressure with diethyl ether as solvent; 0.02 mol% Rh₂O₃ and 1.7 mol% of R₃P were employed. The active catalyst was preformed by heating the mixture to 150°C for 30 minutes. After a reaction period of 3 hours, 80–90% yields of hydroformylation products were obtained, which consisted of 58 mol% C₅ monoaldehydes and 42 mol% C₆ dialdehydes. The composition of the C₅ fraction was 96% *n*-valeraldehyde. The composition of the C₆ dialdehyde fraction was as follows: 58% 2-methyl-1,5-pentanedial; 29% 2-ethyl-1,4-butanediol; 9% 1,6-hexanediol; and 4% not identified.

The following scheme was proposed for the possible reaction pathway, especially in the presence of a large excess of phosphine (96):



In a further study, Fell and Bahrmann (97) explored the effects on reaction rate and product distribution of trialkylphosphines and phospholanes with varying steric and electronic effects. The ligand cone angle (98) was used as a measure of steric bulk, and for electronic effects the $\Sigma x(i)$ value was chosen. The results indicated that neither of these two criteria was exclusively responsible for the catalytic activity of the phosphine-substituted catalysts. Triisopropylphosphine gave the highest reaction rate, a high overall yield, and a high percentage of dialdehyde, yet it was an intermediate phosphine with respect to both steric and electronic properties. The combination of these two factors, termed "complex basicity" (99), gave a somewhat better correlation with the results obtained but was not completely satisfactory.

A two-stage process for the hydroformylation of butadiene to give good yields of a desired product—1,6-hexanediol—has been described (100). The first stage employed [(C₆H₅)₃P]₂Rh(CO)Br and excess triphenylphosphine as catalyst and reaction conditions of 120°C and 200 atm of 1/1 H₂/CO in methanol as solvent. The principal product was 3-penten-1-al dimethyl acetal. This was treated with 1,3-propanediol to form a cyclic acetal, then hydroformylated with Co₂(CO)₈ and dodecyl-9-phospha-9-bicyclononane at 170°C and 80–110 atm of 2/1 H₂/CO. The product of

this step was hydrogenated over Raney nickel to give a high yield (82%) of 1,6-hexanediol.

VI

CATALYST SEPARATION AND RECYCLE

An aspect of the hydroformylation reaction which is of particular importance in continuous commercial operation is the separation of the catalyst from product aldehyde and/or alcohol, together with its recovery and recycle into the reactant stream. This feature is of considerable economic and process importance for cobalt reactions and of extreme economic importance for rhodium reactions.

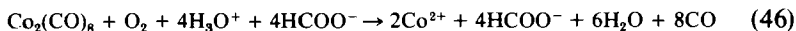
Cobalt hydrocarbonyl is a volatile substance of limited stability at or above ambient temperature. Its tendency to decompose at undesirable sites in a process has posed a severe problem for commercial operations. Consequently, the patent literature contains numerous references to a variety of schemes for selectively removing cobalt from product and converting it to a form suitable for catalytic reuse.

Some of the more prominent schemes for cobalt removal and recycle are:

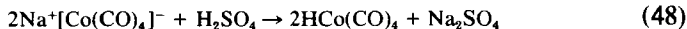
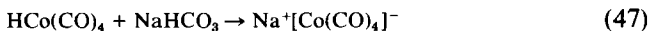
1. Reaction with aqueous acid to form cobalt salts suitable for reuse.



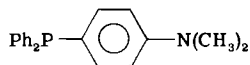
2. Extraction with aqueous acid accompanied by oxygen (46).



3. Extraction of the highly acidic cobalt hydrocarbonyl by aqueous base then phase separation from product, followed by acidification to reform the hydrocarbonyl catalyst.



A method for separating rhodium catalyst from product has involved functionalization of phosphine ligands. In one proposed scheme, a triarylphosphine ligand was prepared which contained an *N,N*-dimethylamino group attached to phenyl (101). This ligand was used with rhodium to effect hydroformylation. The product solution was extracted with aqueous acid to transfer both metal catalyst and ligand to the aqueous phase. The catalyst was then regenerated by neutralization and extraction with organic solvents.



In another study (102), a triarylphosphine with a sulfonyl group on each phenyl was prepared and used with rhodium in a buffered aqueous system. The hydroformylation of propylene was conducted at 80°C and 50 atm of synthesis gas. The yield of aldehydes was 98% on converted propylene with an *n*:iso ratio of 6.7:1.

In rhodium hydroformylations, highly efficient separation and recovery of catalyst becomes imperative, because of the very expensive nature of the catalyst. Any loss, by trace contamination of product, leakage, or otherwise, of an amount of rhodium equivalent to 1–2 parts per million (ppm) of aldehyde product, would be economically severe. The criticalness of this feature has contributed to some pessimism regarding the use of rhodium in large hydroformylation plants (63). However, recent successful commercialization of rhodium-catalyzed processes has proved that with relatively simple process schemes losses are not a significant economic factor (103, 104).

VII

HETEROGENEOUS CATALYSTS

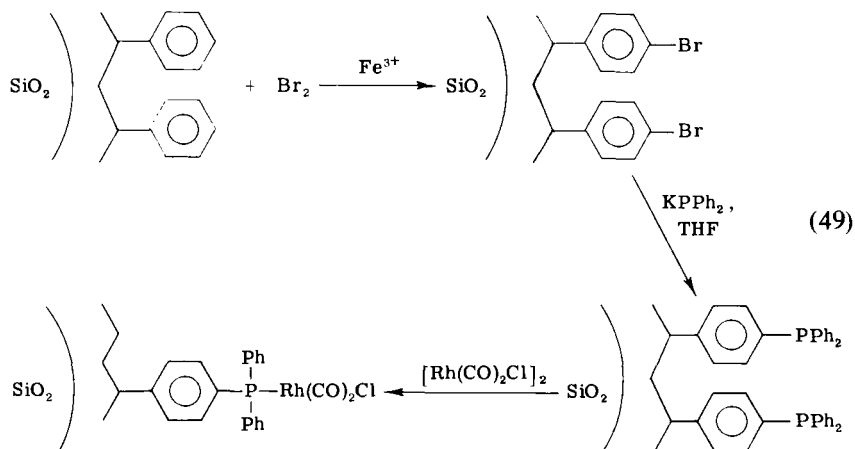
Much effort has been devoted to the conversion of homogeneous hydroformylation catalysts to heterogeneous catalysts. This would have immediate application for product–catalyst separations. The process could be either vapor-phase (especially suitable for lower molecular weight aldehydes) or liquid-phase with suspended insoluble catalysts. In addition, chemical bonds between metal catalysts and inert supports can be accomplished by attachment of a complexing group (e.g., phosphine) to the support. The objective has been to optimize and retain the positive benefits of the heterogeneous system without losing the intrinsic benefits of greater activity and selectivity of homogeneous catalysis. Although many interesting and useful results have been obtained, it is not indicated at this point in time that complete success has been accomplished.

Among the earliest studies was that of Moffat (105). Poly-2-vinylpyridine, cross-linked with 4–8% divinylbenzene, was used as the coordinating support. The amount of cross-linking was found to be critical: too little gave a soluble polymer, while too much gave an intractable material which absorbed little metal. Cobalt was used as the catalyst, and the reaction was conducted at 150°–200°C and 2000–3000 psi of 1/1 H_2/CO .

It was concluded that in this case an equilibrium existed which gave 100 ppm of soluble cobalt at reaction temperature. The polymer support acted as a reservoir for furnishing soluble metal at reaction temperature and reabsorbing it after completion (about 10 ppm in the product after cooling to ambient temperature). The rate approximated that obtained in a standard cobalt reaction with 100 ppm of cobalt catalyst.

Allen (106) also studied cobalt hydroformylation with a polymer-bound catalyst. The polymer was formed from diphenyl-*p*-styrylphosphine cross-linked with divinylbenzene. 2-Hexene was the substrate, and reaction conditions were 175°C and 1500–3000 psi of 1/1 H₂/CO. The product aldehyde was 55% linear, and the effluent product solution contained 20–50 ppm cobalt.

Most of the more recent studies have concentrated on rhodium. An effective system for a gas-phase reaction was reported by Arai *et al.* (107). The catalyst support was silica gel, which was desirable for its high surface area properties (293 m²/g). This was covered with a polymer formed from styrene and divinylbenzene, either by emulsion (A) or by solution (B) polymerization. Each of these base materials was then functionalized by the reactions shown in Eq. (49).



The catalyst formed in this manner exhibited carbonyl infrared absorptions, as shown in Table XXX. These catalysts were tested by hydroformylation of ethylene or propylene at 100°C and atmospheric pressure. Both were effective, with (A) being better than (B), probably because of the higher surface area. The aldehyde formed from propylene was a mixture of 63% *n*- and 37% isobutyraldehyde. The rate expression for ethylene hydroformylation was:

$$\text{rate} = k[\text{H}_2][\text{C}_2\text{H}_4][\text{CO}]^{-0.5}$$

TABLE XXX
PROPERTIES OF SILICA-POLYSTYRENE
FUNCTIONALIZED CATALYSTS (107)

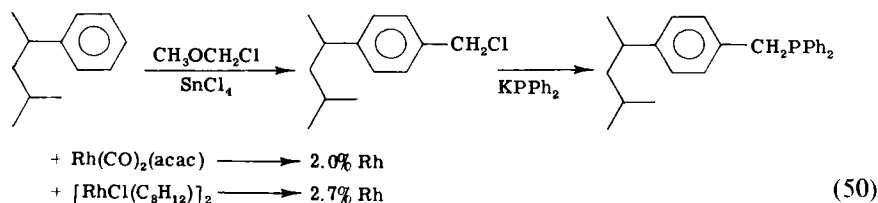
	Type A	Type B
ν_{CO} (cm^{-1})	2080	2075
	2020	1995
% Rh	8.2	6.5
Surface area (m^2/g)	42	9.8

The beneficial effect of phosphine linkage was demonstrated by comparison with catalysts formed by direct deposition of $(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{Cl}$ or RhCl_3 on silica. These materials exhibited negligible activity under the cited conditions.

However, $(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{Cl}$ on alumina or activated carbon were effective hydroformylation catalysts under more severe conditions (108). At 148°C and a pressure of 49 atm (CO 37.5 mol%, H_2 37.5, propylene 25), good activity was found. The propylene conversion was 30% at a contact time of 0.92 cm^3 of reactor void space/ cm^3 of feed per minute. Isomer ratios of 1.3 to 1.9:1 *n*:iso were realized. By-product formation was low, with <1% conversion to alcohols plus alkanes and 2.2% high-boiling materials. This system was stable for a 300 hour operating time, with no detectable loss of activity or selectivity.

Polymers containing a benzyldiphenylphosphine complexing group are also effective. Capka *et al.* (109) studied the catalyst formed from this type of organic substrate and $\text{RhCl}_y(\text{C}_2\text{H}_4)_z$. 1-Hexene was hydroformylated with 40 atm of 3/4 H_2/CO to produce 56% *n*-heptaldehyde and 24% 2-methylhexaldehyde. Significant isomerization to internal olefins also occurred.

Allum and co-workers (110) studied several polymer types and focused on macroreticular, high surface area, cross-linked polystyrene. The best polymer found was AMBERLITE XAD-2, spherical beads with a high surface area of $120 \text{ m}^2/\text{g}$. A linkage for rhodium was provided by attachment of a $-\text{CH}_2\text{PPh}_2$ group:



The catalyst containing 2.0% Rh, insoluble in organic solvent, was used for hydroformylation of 1-hexene at 80°C and 43 atm of 1/1 H₂/CO. The catalyst "concentration" was 1 mmole Rh per mole of olefin. After 4 hours a 41% yield of aldehyde was obtained, with a 2.5:1 isomer ratio. Some isomerization to internal olefins also occurred. A significant feature was the rhodium concentration of 2 ppm in the product.

Application of a novel concept of liquid-loaded catalyst solutions on inert supports (111-113) gave an increased reaction rate over the corresponding catalyst-on-support alone. For example, a solution of (Ph₃P)₂Rh(CO)Cl and excess triphenylphosphine in butylbenzyl phthalate was added to silica gel. The liquid loading was critical. Small amounts gave low reaction rates, whereas excessive loading caused blockage of the pores in the silica gel and reduced the effective surface area, again causing decreased rates. Thus, conversion as a function of loading passed through a maximum. Reaction conditions were 148°C and 700 psi. Low isomer ratios of 2.7:1 were obtained, even with excess triphenylphosphine present.

Investigations have shown that polymer-bound rhodium hydroformylations respond to reaction parameters in a manner similar to the homogeneous counterparts, although some departures occur (114). Phosphinated polystyrene supports were prepared from styrene-divinylbenzene resins (1% divinylbenzene, BIORAD SX-1, 200-400 mesh, 14,000 mol wt. exclusion limit). Rhodium was then attached by thermal phosphine exchange from HRh(CO)(PPh₃)₃, followed by Soxhlet extraction. In order to examine the effects of excess phosphine on reaction rates and product composition, a series of resins with varying phosphorus and metal content was prepared. Best results were obtained with a resin in which 40% of the phenyl groups were phosphinated (%P = 7.01) and in which the P/Rh ratio after metalation was 19. Nearly quantitative yields of hexaldehydes with selectivities of up to 94% linear isomer were obtained from 1-pentene. It was speculated that the high phosphine content favored the bistriphenylphosphine species in the equilibrium shown in Eq. (51), and thus favored the associative mechanism postulated by Wilkinson (24). A summary of results obtained with the high-phosphorus polymer and a comparison with homogeneous rhodium under similar conditions are given in Table XXXI.

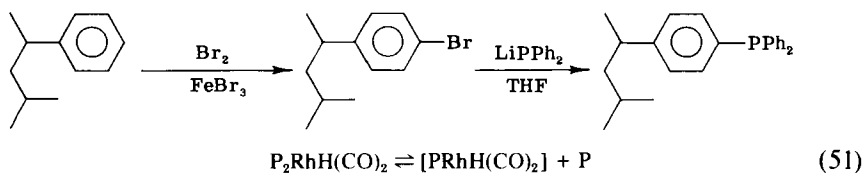


TABLE XXXI
HYDROFORMYLATION OF 1-PENTENE CATALYZED BY $\text{P}^-(\text{PPh}_2)_3\text{RhH}(\text{CO})$,^a COMPARED
WITH HOMOGENEOUS $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ ^b (114)

Temp (°C)	Pressure (psi)	Catalyst P ^c		Catalyst H ^c	
		Yield (%)	Selectivity ^d	Yield (%)	Selectivity ^d
50 ^e	400	35	5.1		
60	400	60.5	5.3	99.7	3.1
80	400	96.2	5.5	99.8	2.9
100	400	97.6	6.1	100	2.9
120	400	98.1	6.0	99.8	2.7
140	400	95.9	6.1	96.2	2.4
160	400	90.8	5.7		
100	800	98.6	4.3	99.7	2.8
100	600	98.3	4.6	99.6	2.8
100	400	97.6	6.2	100	2.9
100	200	95.9	8.8	98.3	3.2
100	100	96	12.1	93.7	3.3
60	100	62.7	9.6	99	3.6
80	100	96.1	12.6	98.7	3.8
100	100	92.4	12.1	93.7	3.3
120	100	94.2	16.1	90.5	2.2
140	100	57	10.2	48.6	2.3
140	200	87	8.7		
140	400	95.9	6.1		
140	600	97.5	4.4		
140	800	98.2	4.3		

^a Polymer-bound catalyst.

^b $4.58 \times 10^{-3} M$ Rh; 400:1 olefin:Rh; 19:1 P:Rh.

^c Catalyst P, polymer-bound; catalyst H, homogenous.

^d Selectivity is the ratio of linear to branched aldehydes.

^e Boldface numbers denote variable being changed.

Although the results with polymer-attached phosphine ligands gave good general trends, some questions need further investigation. Data concerning metal elution during reaction are highly desirable. While it was shown that the catalyst could be recycled, elemental analysis for rhodium before and after reaction (115) is not sufficient for noble-metal catalysis evaluation. The effects of diffusion, especially at low pressure and high temperature, would be expected to be significant and may obscure or mislead interpretation. The presence of unreacted halogen in the polymer, noted in one instance (116), could also alter catalytic properties.

The important factor of rhodium elution from polymer-bound catalysts

was the subject of a recent study (117). The rhodium concentration in solutions over these catalysts was measured as a function of metal loading, temperature, solvent, and partial pressures of hydrogen and carbon monoxide. The ligand-substituted supports were all porous, macroreticular, styrene-based polymers, cross-linked with divinylbenzene or with ethylene glycol dimethacrylate. Amine resins were polymeric analogs of *N,N*-dimethylbenzylamine and contained 5.8% nitrogen. Phosphine resins were analogs of dibutylphenylphosphine and contained 6.6–9.7% phosphorus. Rhodium was attached by a bridge-splitting reaction between the polymer-attached ligand and rhodium carbonyl chloride. Rhodium levels were kept sufficiently low that the ligand:Rh ratio was at least 10.

The experiments were conducted in a down-flow tubular reactor with continuous feed and product withdrawal. For phosphine resins, establishment of equilibrium was exhibited by the fact that rhodium concentrations in solution were proportional to percent loading. The concentration was also dependent on solvent. As the solvent polarity increased, rhodium concentration increased. Typical concentrations in the effluent were $0.2\text{--}2.0 \times 10^{-5} M$ Rh for reaction at 85°C , 1500 psi 1/1 H_2/CO . An increase in CO pressure increased the concentration of rhodium in solution, and an increase in temperature sharply decreased the metal concentration. These are understood as factors that influence the equilibrium between phosphine and carbonyl complexes.

For amine resins, an additional implication was the fact that partial reduction of aldehyde to alcohol occurred and further changed the solvent polarity. Some pertinent data are summarized in Table XXXII.

TABLE XXXII
RHODIUM ELUTION AND PRODUCT COMPOSITION FROM AMINE RESIN
CATALYSTS^a (117)

[Rhodium] (<i>M</i>)	Loading (%)	Conversion (%)	Alcohol (%)	[Rh]:Loading
1.3×10^{-5}	0.23	40	5	5.7×10^{-5}
4.0×10^{-5}	0.72	15	Low	5.6×10^{-5}
5.5×10^{-5}	0.92	30	Low	6.0×10^{-5}
14.0×10^{-5}	1.4	35	Low	10.0×10^{-5}
12.0×10^{-5}	2.0	20	Low	6.0×10^{-5}
17.0×10^{-5}	2.0	25	Low	8.5×10^{-5}
0.5×10^{-5}	0.23	65	25	2.2×10^{-5}
1.5×10^{-5}	1.25	80	65	1.2×10^{-5}

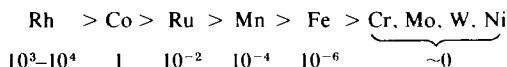
^a Substrate, 1-hexene; temperature, 100°C ; pressure, 1000–2000 psi 2/1 H_2/CO .

At low conversions (aldehyde product) the ratio of rhodium in solution to percent loading remains fairly constant over a tenfold range of loading. At higher conversions, with increasing alcohol content and resultant change in polarity, the ratio decreases.

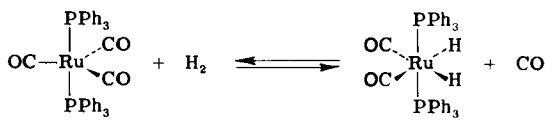
VIII

CATALYSTS OTHER THAN COBALT AND RHODIUM

While cobalt and rhodium have been the focus of most research and are the metals of choice for commercial hydroformylation reactions, numerous other metals have been disclosed as catalysts in the patent literature. However, only some of the carbonyl-forming metals can be seriously considered. Even of these, a comparison of relative reactivity (118) based on cobalt as the standard indicates a decided preference for only two or three metals. This listing may be considered incomplete without the inclusion of platinum and copper, which have recently received significant attention (*vide infra*).



Ruthenium has been studied by Wilkinson and co-workers (24, 36, 119) and by Schulz and Bellstedt (120). The Wilkinson group studied the ruthenium system in much detail. In a typical example, 1-hexene was hydroformylated under 100 atm of hydrogen and carbon monoxide, benzene solvent, with $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ as catalyst at 120°C. In a period of 20 hours, 86% conversion of the olefin occurred, with 99% selectivity to aldehydes. The ratio of linear to branched aldehydes was 2.4:1. The actual catalyst was concluded to be $\text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2$. An increase in hydrogen partial pressure increased the rate of reaction, whereas an increase in the partial pressure of carbon monoxide decreased the rate. This agrees with a first step consisting of the oxidative addition of molecular hydrogen to tricarbonylbis(triphenylphosphine)ruthenium, with a simultaneous loss of a carbon monoxide ligand.



An induction period was noted unless $\text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2$ was preformed, in which case none occurred. Conditions for optimum results were crit-

ical. The optimum temperature was 120°C; above 150°C, conversion decreased and mixtures of ruthenium complexes were recovered from the reaction mixture. High hydrogen partial pressures gave increased rates, but 2/1 H₂/CO gave 35% hydrogenation to hexane. Excess triphenylphosphine produced higher isomer ratios (up to 5:1) but drastically decreased the reaction rate (<10% conversion in 20 hours with molten triphenylphosphine as solvent).

The mechanism was similar to those involving cobalt and rhodium, and is depicted in Fig. 10.

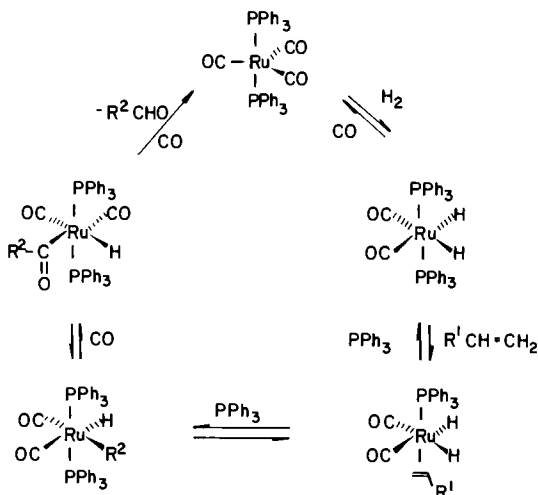
The trinuclear species Ru₃(CO)₁₂ was less active as a catalyst unless triarylphosphines or triaryl phosphites were added, in which case the activity was greater than that of the mononuclear species. The catalytic polynuclear species was probably H₄Ru₄(CO)₈L₄.

Platinum, as [(Ph₃P)₃PtH]⁺PF₆⁻, showed a low activity for converting olefins to aldehydes (121). At 150°C, 1500 psi H₂/CO, 5 hours reaction time, 16% of 1-hexene was converted to a mixture of aldehydes and alcohols.

Somewhat better results were obtained by the use of (Ph₃P)₂PtI₂ in a polar solvent such as dimethylformamide (122). At 180°C and 250 atm H₂/CO, an 89% conversion to aldehydes with an isomer ratio of 4.3:1 was obtained in 1 hour. Relatively high concentrations of catalyst (2500 ppm as Pt metal) were required. Palladium, as (Ph₃P)₂PdI₂, was less effective and also produced considerable amounts of lactones.

The most striking results have been obtained with platinum complexes which contain SnCl₃⁻ as ligand. Hsu and Orchin (123) described the catalyst as PtH(SnCl₃)(CO)(PPh₃)₂. It was active at 100°C and 3000 psi synthesis gas. Significantly, the aldehyde product from 1-pentene was 95% hexanal. Due to the fact that the catalyst was relatively unstable, in that it lost CO on drying or extruded CO and SnCl₂ on recrystallization, it could not be examined in detail but was thought to be either [Pt(H)(CO)(PPh₃)₂]⁺SnCl₃⁻ or a nonionic five-coordinate complex.

Schwager and Knifton (124, 125) studied a catalyst system containing platinum(II) chloride, tin(II) chloride, and triphenylphosphine. The catalyst system was effective for linear α-olefins, branched-chain α-olefins, and internal and cyclic olefins with more stringent conditions. Solvents of intermediate polarity such as acetophenone or methyl isobutyl ketone were preferred. Highly polar solvents, e.g., dimethylformamide or acetonitrile, inhibited the reaction. The most effective catalyst composition was that which contained 5Sn:2P:1Pt. The excess SnCl₂ was needed to maintain catalyst stability. Temperatures of 65°–100°C gave good product distribution and rate, while temperatures above 100°C gave excessive olefin isomerization and some catalyst decomposition. In a typical ex-



periment at 66°C, 1500 psi H₂/CO, and methyl isobutyl ketone as solvent, 1-heptene gave an 85% yield of aldehyde with 90% selectivity to the linear aldehyde. The yield of isomerized olefin was 3.6% and of heptane was 2.7%.

The reaction was stated to proceed by means of an associative mechanism, similar to the one proposed for the rhodium–triphenylphosphine system, with $\text{HPt}(\text{CO})(\text{SnCl}_3)(\text{PPh}_3)$ as the active intermediate. The high selectivity to linear aldehyde was attributed to steric requirements. The kinetic data led to the following general rate expression:

$$\frac{d(1\text{-octanal})}{dt} = \frac{K \cdot [\text{Pt}]^{1.5} [1\text{-heptene}] [P_{\text{H}_2}]}{[P_{\text{CO}}]^{0.5}}$$

This is similar to kinetic expression for other transition metal-catalyzed hydroformylations, except for the unusually high dependence on metal concentration.

Copper, and occasionally silver, have been used as catalysts for hydroformylation of α -olefins. Phosphite complexes of copper(I) chloride have been claimed as catalysts (126). Phthalocyanine complexes of Group IB metals have been stated to show a low degree of catalytic activity (127). One of the more interesting examples of copper catalysis was disclosed by McClure (128). Copper powder, with a controlled amount of water (0.2–4.0 moles H_2O /mole Cu), gave a slow conversion of pro-

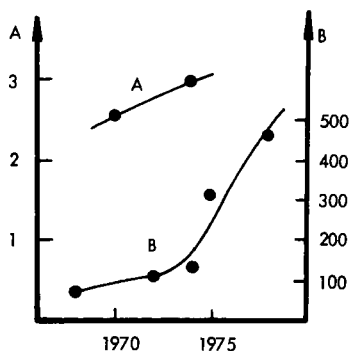


FIG. 11. Growth patterns for cobalt and modified metal commercial hydroformylations (118). (A) Total production volume, 10^6 tons/year. (B) Production by modified catalysts, 10^3 tons/year.

TABLE XXXIII
PRODUCTS OF COBALT AND MODIFIED RHODIUM PROCESSES FOR
BUTYRALDEHYDE

	Cobalt (129)	Rhodium-triphenylphosphine (103,104)
Aldehydes ^a	78–82%	97–98%
Alcohols	10–12%	Nil
Butyl formate	2%	Nil
Propane	2%	2%
Others	6–8	< 1%

^a Efficiencies are based on converted propylene.

TABLE XXXIV
RAW MATERIAL REQUIREMENTS FOR CONVENTIONAL COBALT
AND MODIFIED RHODIUM PROCESS^a (103)

	Rhodium	Conventional
Propylene (94%) (kg)	750	930
Synthesis gas (nm ³)	740	1200

^a Units are per 100 kg of *n*-butyraldehyde.

pylene at 195°–200°C. The product consisted of 98% aldehydes with 60% *n*-butyraldehyde composition.

IX

COMMERCIAL TECHNOLOGY TRENDS

To date, unmodified cobalt hydroformylation processes produce most of the aldehydes and/or alcohols which comprise the 8–10 billion pounds of commercial products made annually. During the 1960's the trialkylphosphine-modified cobalt system was adopted in some new plants, particularly for detergent-range alcohols. The 1970's has seen the advent of rhodium technology for butyraldehyde and propionaldehyde. A growth curve for the modified catalysts and conventional cobalt processes has been published (118), as shown in Fig. 11. Although these data are probably conservative, they serve to illustrate the relative growth rates during recent years.

In view of rapidly increasing raw material prices and plant construction costs, as well as more stringent environmental standards, it is likely that future practices will favor high-efficiency processes which operate under mild reaction conditions with few by-products. Modified rhodium is advantageous in these respects, as shown in Tables XXXIII and XXXIV. In view of the recent successes with commercial rhodium systems (103, 104, 130, 131), it is likely that these will find more extensive use in the next few years.

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The Fischer-Tropsch Reaction

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I

INTRODUCTION

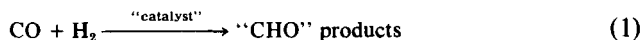
The drastic sixfold increase in oil prices since the end of 1973, coupled with world-wide concern regarding the rapid depletion of oil and natural gas reserves, has led to a reassessment of the role of coal as a major world energy source. In the 1972 Club of Rome's report, *Limits to Growth*, it was concluded that oil reserves would be exhausted within 20 years, natural gas within 22 years, and coal within 110 years. Although it now appears that these estimates err rather on the side of pessimism, there is general agreement that, at current rates of consumption, the world's oil and natural gas reserves could be largely exhausted by the end of the first quarter of the 21st Century. At the current rate of energy consumption, the amount of coal presently available in the United States will be sufficient to supply that country's needs for about 300 years (1).

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In 1974 this quantity was estimated to constitute about 27% of the total world supply (2).

The most direct method of using coal as an energy source is combustion; however, except in large installations such as power stations, coal is not an ideal fuel. It usually burns less cleanly than either oil or gas, and the cost of bulk transportation is considerably greater for coal than for oil. Furthermore, the vast world-wide refining capacity built up during the last 30 years cannot, in the short term at least, be converted to process coal rather than oil. Success in exploiting the world's huge reserves of coal will depend in the long run on developing technology to convert coal into liquid products and gas (3). One method of accomplishing the goal is via the Fischer-Tropsch synthesis, in which synthesis gas—a mixture of carbon monoxide and hydrogen produced by burning coal in the presence of oxygen and steam—is converted into a wide range of hydrocarbon products.

The Fischer-Tropsch synthesis, which may be broadly defined as the reductive polymerization of carbon monoxide, can be schematically represented as shown in Eq. (1). The "CHO" products in Eq. (1) are any organic molecules containing carbon, hydrogen, and oxygen which are stable under the reaction conditions employed in the synthesis. With most heterogeneous catalysts the primary products of the reaction are straight-chain alkanes, while the secondary products include branched-chain hydrocarbons, alkenes, alcohols, aldehydes, and carboxylic acids. The distribution of the various products depends on both the type of catalyst and the reaction conditions employed (4).



It is not the intention of this article to concentrate on classical Fischer-Tropsch systems involving heterogeneous catalysts, for these have been well described elsewhere (4-10). Instead, we intend to focus on homogeneous systems which are either capable of catalyzing the reactions between carbon monoxide and hydrogen or which provide some insight into how these two molecules can be induced to interact at a metal center(s). In order to provide a background to further discussion, we include a short historical survey, together with a description of the present commercial application of the process as practiced in South Africa. In Section IV some new heterogeneous catalyst technology is briefly reviewed.

A. Historical Survey

The history of the Fischer-Tropsch synthesis can be traced back to 1902, when Sabatier and Senderens (11) reported that certain heteroge-

neous nickel systems catalyzed the reduction of carbon monoxide to methane (4). Some ten years later several patents appeared from the *Badische Anilin und Soda Fabrik* in which it was disclosed that, in the presence of alkali-activated cobalt and osmium oxides supported on asbestos, carbon monoxide and hydrogen react together at 100–200 bar/300°–400°C to give a liquid product containing alkanes, alkenes, alcohols, aldehydes, ketones, and acids (12). In 1923 Fischer and Tropsch reported an analogous high-pressure reaction using alkalized iron turnings as catalyst (13). It is this latter observation which has led to the development of the modern Fischer-Tropsch catalysts.

Probably the most significant breakthrough came in 1925, when Fischer and Tropsch reported the first catalyst, an iron oxide/zinc oxide system, capable of producing higher hydrocarbons from carbon monoxide and hydrogen at atmospheric pressure (14). Extensive catalyst research over the next ten years led to the development of the Co-ThO₂-MgO-kieselguhr catalyst and the commissioning, by Ruhrchemie in 1936, of the first commercial Fischer-Tropsch plant. During the next five years 15 plants came onto stream, nine in Germany, four in Japan, and one each in France and Manchuria. At the height of production in 1943, the German plants were turning out 585,000 metric tons of products consisting of 46% gasoline, 23% diesel oil, 3% lubricating oil, and 28% waxes, detergents, synthetic fat and oil (5). All these plants used the cobalt-based catalysts, because originally the process had been developed to operate at atmospheric pressure and under such conditions cobalt is superior to iron. As a consequence of the war effort, supplies of cobalt became scarce in the early 1940's, and impetus was thus added to the development of iron catalysts to replace cobalt.

The two important discoveries in the search for iron-based Fischer-Tropsch catalysts were (a) the finding that the addition of alkali yielded significant improvements in the activity and selectivity (to liquid products) of iron catalysts (15), and (b) the development of the medium-pressure synthesis (16). In 1943 a pilot plant was constructed at Schwarz-Leide in Germany for the comparative testing of iron-based catalysts. However, the outcome of World War II curtailed its activities. After 1945 many of the plants were destroyed and, for those remaining, recommencement of operation was forbidden for several years. Of the three plants restarted, the last at Bergkamen was closed in 1962.

Iron-based catalysts have been used in all the plants constructed after the war, because; (a) iron is considerably cheaper than cobalt, (b) iron systems are generally more stable, and (c) greater flexibility with regard to product distribution can be attained. With the exception of the SASOL complex, which will be dealt with in Section I,B, the only Fischer-Tropsch plant of any appreciable size constructed in the West since the

end of World War II (no accurate data are presently available for Eastern bloc countries) was that built by Carthage Hydocol Co. at Brownsville, Texas. This plant was designed to produce 360,000 tons/yr of liquid fuels and 40,000 tons/yr of chemical products using synthesis gas produced from natural gas by partial oxidation, but because of myriad technical difficulties it never entered full commercial service and was eventually closed in 1957 (5).

The advent of cheap oil in the 1950's, coupled with escalating coal costs, finally diverted interest from the Fischer-Tropsch synthesis as a commercial proposition in western Europe and America. Until recently, the only noncommunist country which has actively pursued Fischer-Tropsch technology has been South Africa.

B. Fischer-Tropsch Today

There are two main reasons for the economic importance of Fischer-Tropsch production in South Africa: (a) the existence there of extremely large coal deposits which can be mined at low cost, and (b) that nation's wish to become independent of external oil supplies.

In 1951, when construction of the SASOL (*Suid-Afrikaanse Steenkool-, Olie-en Gaskorporasie Beperk*) complex was started, the above two reasons were peculiar to South Africa. Now that oil supplies have entered the political arena, more countries are questioning their dependence on external supplies and national energy programs are placing increasing emphasis on the need for a degree of self-sufficiency in this area.

The SASOL-I complex (17), which is shown schematically in Fig. 1, began operating in 1955 and, in 1957, reached its planned output of 233,000 tons of primary products per year. In 1966 its output was increased to 240,000 tons (17a). SASOL-I incorporates two types of reactors, both using iron-based catalysts. One operates at 25 bar/220°–240°C with an H_2/CO ratio of 1.7:1 and produces a C_5+ product consisting of 32% gasoline, 21% diesel fuel, and 47% higher paraffins. The second type of reactor, operating at a higher temperature (320°–340°C) with a hydrogen-rich syngas ($H_2:CO = 3.5:1$), produces nearly 70% of gasoline fuel (18). Recently, South Africa has announced the construction of a \$1 billion complex, SASOL-II, which, when it reaches completion in the 1980's, will be capable of producing 1,500,000 tons/yr of Fischer-Tropsch products, thereby supplying about 40% of the present daily requirements for motor fuel in South Africa (19).

With regard to the rest of the world, the situation is less clear-cut.

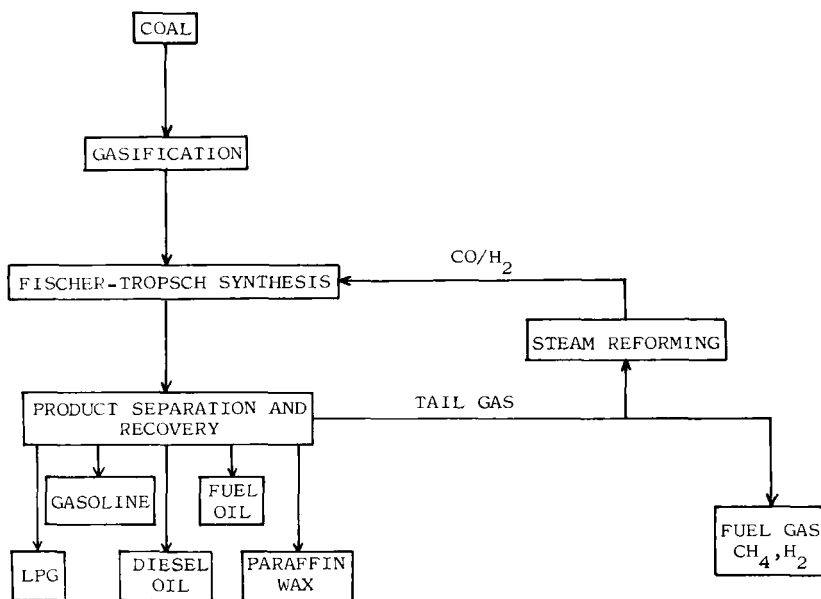


FIG. 1. Schematic representation of a commercial Fischer-Tropsch complex.

Although there is quite a strong research effort in both the private and governmental sectors, especially in the United States, no firm plans to construct commercial Fischer-Tropsch plants have been announced. Nevertheless, several coal-conversion pilot plants are in an advanced stage of development, and conceptual designs, together with economic evaluations, have been produced for plants capable of processing 140,000 tons of coal per day (20). Such plants would involve a fixed capital investment of some \$2.8 billion (1975 estimate) (21).

C. The Role of Homogeneous Catalyst Systems

In view of the size of operation being contemplated, it is unlikely that homogeneous catalysts will play a primary role in the production of synthetic oil. However, from the standpoint of the chemical industry, the complex mixture of products obtained from the classical Fischer-Tropsch process is generally unattractive owing to the economic constraints imposed by costly separation/purification processes. What is needed is a catalyst system for the selective conversion of CO/H₂ mixtures to added-

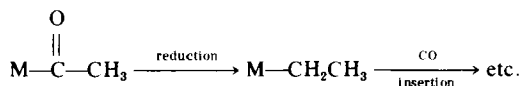
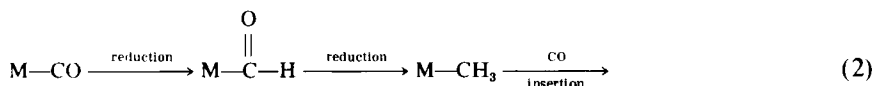
value chemicals. A standard definition of an added-value chemical, in terms of carbon monoxide and hydrogen, bearing in mind the present economic climate, is that it is one which retains at least one of the oxygen atoms of the original CO/H₂ reactants. A chemical of immediate appeal is ethylene glycol, because the present process starts with ethylene which is first converted to ethylene oxide and then hydrolyzed to ethylene glycol. A direct route from syngas, under readily realizable conditions of temperature and pressure, would offer a considerable saving. One of the commercial routes to acetic acid is via the carbonylation of methanol using a soluble rhodium catalyst (22). Because methanol is currently produced from synthesis gas (23), a direct route from CO/H₂ to acetic acid would clearly be attractive. Similarly, a direct route to ethanol could be expected to undercut the present process involving the hydration of ethylene.

The key factor in any CO/H₂-to-chemical process is selectivity, and it is here that homogeneous systems could play an important role. There are many examples of slight ligand modification leading to impressive selectivity improvements in homogeneous transition metal-catalyzed reactions (24). Often, homogeneous catalysts function under milder conditions than their heterogeneous counterparts; and with escalating energy costs, this consideration will assume increasing importance in assessing the overall economics of a given process. Furthermore, many reactions between CO and H₂ are highly exothermic, a fact which can lead to heat-transfer problems in the industrial application of heterogeneous systems. The use of soluble catalysts would go a long way toward alleviating these problems. Finally, homogeneous catalysts are generally more amenable to study than heterogeneous systems. Problems of catalyst surface and sites of widely differing activity are not encountered, and thus detailed mechanistic studies are possible which will, hopefully, lead to a better understanding of reaction parameters and to the design of new highly active and selective catalysts.

II

FISCHER-TROPSCH RELATED ORGANOMETALLIC CHEMISTRY

The intention of this section is to discuss some aspects of the chemistry of metal complexes in solution which are related to the conversion of carbon monoxide and hydrogen to organic products. In order to provide a framework for the initial part of the discussion, we have adopted the simple reduction/insertion sequence shown in Eq. (2).

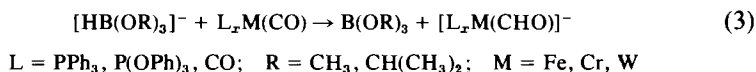


In such a sequence the first complex incorporating the elements H, C, and O is a metal formyl species; in Section II,A we describe the preparation and properties of such complexes. In Section II,B, stoichiometric reductions of both metal carbonyl and metal acyl species are presented; and in Section II,C, homogeneous CO/H₂ conversion catalysts are discussed.

A. Metal Formyl Complexes

The first report of a well-characterized metal formyl species appeared in 1973 when Collman and Winter reported that treatment of Na₂Fe(CO)₄ with acetic anhydride gave the formyl complex [Fe(CHO)(CO)₄]⁻, which was isolated as the N(PPh₃)₂⁺ salt (25). In solution the complex underwent slow decarbonylation [*t*_{1/2} (25°C) ≥ 12 days] to yield the hydrido carbonyl species, [FeH(CO)₄]⁻. No evidence was obtained for the reverse reaction, i.e., insertion of CO into the Fe—H bond. In 1976 two further reports of metal formyl species appeared: Casey and Neumann described an elegant route to a wide range of such species via the reaction of metal carbonyl compounds with trialkoxyborohydrides (26) [Eq. (3)], and Collins and Roper reported that the osmium formyl complex, Os(CHO)Cl(CO)₂(PPh₃)₂, could be formed by hydrolysis of the corresponding thioformyl complex (27). In solution at room temperature the formyl complex is unstable; carbon monoxide is rapidly evolved with formation of the hydrido carbonyl species, OsHCl(CO)₂(PPh₃)₂. These authors postulated that the same formyl complex may be involved in the reaction between Os(CO)₃(PPh₃)₂ and HCl which is reported to yield OsCl₂(CO)₂(PPh₃)₂. However, no discussion was included as to how the formyl complex was formed from Os(CO)₃(PPh₃)₂ and HCl. Although protonation of a formyl species to give formaldehyde is a known process (25, 26), it is not clear how protonation of a carbonyl could lead to a formyl species. Such protonation would be expected to occur at the carbonyl oxygen rather than at the carbonyl carbon, and conversion of

an $M-C\equiv\overset{+}{O}H$ species to a metal formyl species has not, to date, been clearly established.



All the above systems represent indirect routes to metal formyl species. At present, there is no proven example of the direct insertion of CO into a metal-hydride bond:



Only the reverse reaction has been observed (*vide supra*).

For the superficially analogous process of carbonyl insertion into a metal-methyl bond,

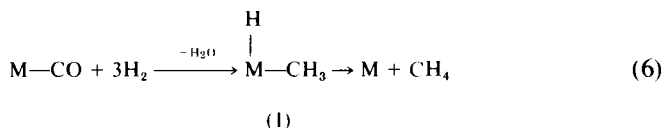


both the forward and reverse reactions are well established for a wide range of transition metals (28). A possible explanation could lie in the relative strengths of a metal-hydride and a metal-methyl bond. There is some evidence to suggest that for a given metal the metal-hydride bond is some 30 kcal/mole stronger than the analogous metal-methyl bond (29, 30). This being the case, and assuming that metal-formyl and metal-acyl bonds are comparable in energy, then the failure to observe reaction (4) is readily understandable. If this difference in bond energy proves to be of general applicability for the Group VIII metals, this would cast considerable doubt on the existence of a "simple" metal formyl intermediate in the Fischer-Tropsch synthesis. Indeed, as will be discussed later, there is a growing body of evidence (albeit indirect) to exclude the occurrence of such an intermediate.

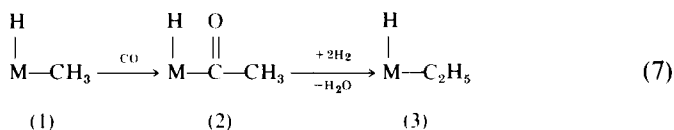
B. Reduction of Coordinated Carbonyl

Methane is always one of the products of any Fischer-Tropsch synthesis and its production from CO may be schematically represented as the formal addition of three moles of hydrogen to a metal carbonyl giving,

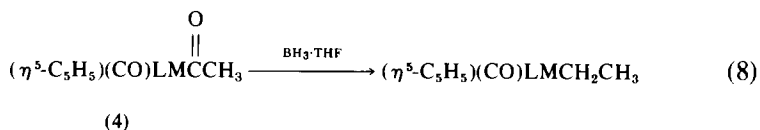
on elimination of water, a methyl hydride species which then reductively eliminates methane, as follows:



Insertion of CO into the metal-methyl bond of 1 followed by reduction and elimination of water would yield a metal ethyl species (3). This latter set of reactions represents, formally at least, a possible growth sequence for the Fischer-Tropsch synthesis.



The stoichiometric reduction of a coordinated carbonyl to methyl was first demonstrated by Treichel and Shubkin in 1968 (31). They reported that treatment of $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3(\text{PPh}_3)]^+$, where $\text{M} = \text{Mo}$ or W , with NaBH_4 in tetrahydrofuran (THF), gave $[(\eta^5\text{-C}_5\text{H}_5)\text{MCH}_3(\text{CO})_2(\text{PPh}_3)]$ in high yield (69% for W and 27% for Mo). Attempts to effect the next reduction in the sequence, i.e., coordinated acyl to ethyl, using NaBH_4 as reductant met with little success (32). However, when BH_3 in THF was used as reductant a smooth reduction was observed (32). Thus, addition of $\text{BH}_3\cdot\text{THF}$ to an acyl complex of type 4 resulted in a rapid (ca. 2 minutes at 20°C) reduction of coordinated acyl to coordinated ethyl, as in Eq. (8):



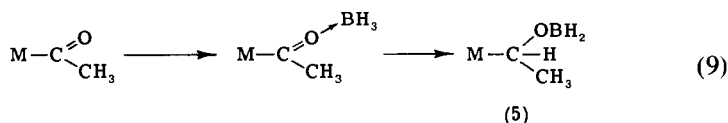
- (a) $\text{M} = \text{Fe}$; $\text{L} = \text{PPh}_3$, PMe_2Ph , $\text{P}(\text{cyclohexyl})_3$, $\text{P}(\text{OPh})_3$, $\text{PPh}(\text{OPh})_2$, $\text{PPh}_2(\text{OPh})$, $\text{P}(\text{CH}_2\text{Ph})_3$, or CO
- (b) $\text{M} = \text{Ru}$; $\text{L} = \text{PPh}_3$

Acyl complexes of a range of transition metals (Pd , Pt , Ir , Co , and Mo) undergo this reduction, although in some cases only indirect evidence could be obtained for the ethyl complex.

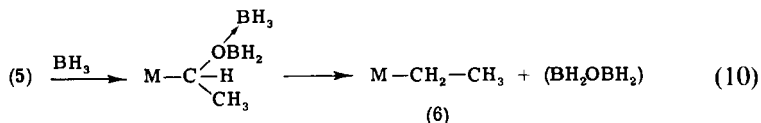
Using $\text{B}_2\text{H}_6/\text{C}_6\text{H}_6$ in place of $\text{BH}_3\cdot\text{THF}$ resulted in a slower reduction and it was suggested that this was due to the lower Lewis acidity of $\text{B}_2\text{H}_6/\text{C}_6\text{H}_6$ compared to $\text{BH}_3\cdot\text{THF}$.

Attempts to effect the reduction using (a) Group IV metal hydrides, e.g., $\text{Et}_3\text{SiH}/\text{CF}_3\text{COOH}$, Ph_3GeH , Ph_2SnH_2 , or Ph_3SnH ; (b) NaBH_4 or LiAlH_4 ; (c) transition metal-hydride complexes, e.g., $\text{HCo}(\text{CO})_4$, $\text{H}_2\text{Fe}(\text{CO})_4$, or $\text{H}_5\text{Ir}(\text{PEt}_2\text{Ph})_2$; or (d) molecular hydrogen in the presence of a transition-metal hydrogenation catalyst, e.g., Pd/C , Pt/C , $[\text{Rh}(\text{norbornadiene})(\text{PMe}_2\text{Ph})_3]\text{PF}_6$, or $\text{RhCl}(\text{PPh}_3)_3$ met with no success. Either no reaction, or decomposition of the acyl complex to ill-defined products, was observed.

In the reaction scheme proposed, the Lewis acidity of the reductant is stressed, and it is suggested that the initial interaction involves BH_3 coordination at the carbonyl oxygen followed by hydride migration to carbonyl carbon to give a species such as 5:



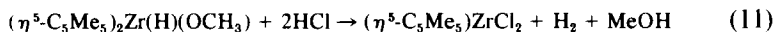
Addition of a second molecule of BH_3 at the oxygen atom of 5, followed by hydride transfer and loss of an oxyborane moiety, is proposed as a route to the metal ethyl complex 6:



Although reaction (8) is thought to represent the first example of the direct reduction of a metal coordinate acyl group, there have been two reports of the reduction of complexes containing groups closely related to acyl: first, the reduction of the salt $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{\text{C}(\text{OC}_2\text{H}_5)\text{CH}_3\}\text{CO}(\text{PPh}_3)]\text{BF}_4$ with NaBH_4 in ethanol to give $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{C}_2\text{H}_5)\text{CO}(\text{PPh}_3)]$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{\text{CH}(\text{OC}_2\text{H}_5)\text{CH}_3\}\text{CO}(\text{PPh}_3)]$ (33); and second, the reduction of compounds of the type $\text{RC}(\text{O})\text{CCO}_3(\text{CO})_9$ with $\text{Et}_3\text{SiH}/\text{CF}_3\text{CO}_2\text{H}$ in THF to give the corresponding alkylidynetricobaltnonacarbonyl complex $\text{RCH}_2\text{CCO}_3(\text{CO})_9$ (34).

In none of the cases discussed above is molecular hydrogen involved. The first report of the stoichiometric reduction of coordinated carbon monoxide by molecular hydrogen is that published by Bercaw *et al.* (35, 36). They reported that mononuclear carbonyl and hydride complexes of bis(pentamethylcyclopentadienyl)zirconium are capable of promoting stoichiometric H_2 reduction of CO to methoxide under mild conditions. Thus, treatment of the dicarbonyl complex $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CO})_2$ with

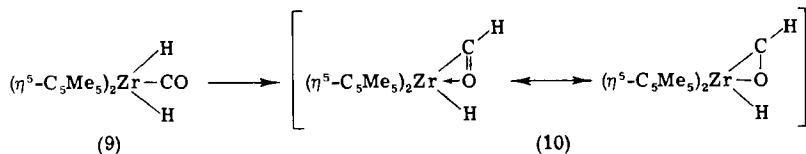
hydrogen (1.5 bar) at either 110° or 25°C in the presence of light (366 nm) results in the quantitative formation of the methoxy-hydrido species $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}(\text{OCH}_3)$ (7). Addition of HCl to 7 gives methanol, hydrogen and the dichloro complex 8:



(7)

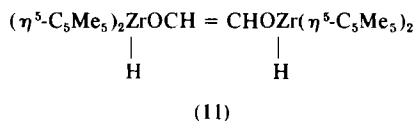
(8)

The reduction to methoxy-hydrido species (7) is thought to proceed via loss of CO from the dicarbonyl complex followed by addition of hydrogen to give the dihydrido carbonyl species (9). The next step suggested (37) is hydride transfer to the carbonyl carbon to give a formyl species in which *both* the carbonyl carbon and the carbonyl oxygen coordinate to the metal center, i.e., 10:

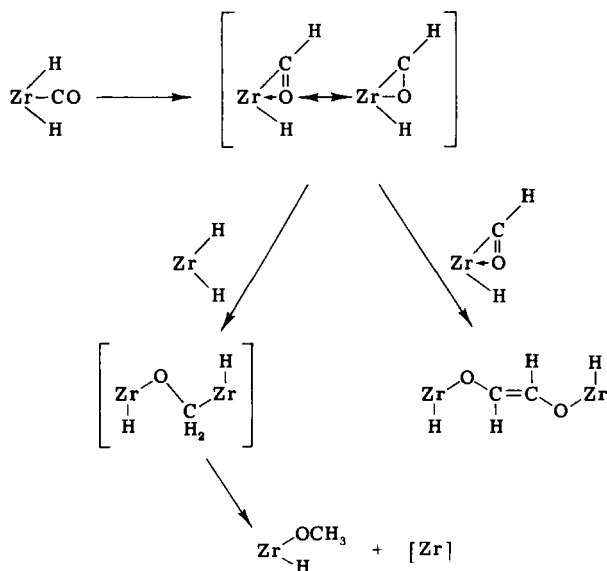


This type of "side-on" bending, which has been established by X-ray crystallographic methods for the related acyl complexes $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{COMe})\text{Me}$ (38) and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{COMe})\text{Cl}$ (39), could overcome the thermodynamic objection, previously discussed, against the formation of a "normal," linearly bonded formyl by CO insertion into a metal-hydride bond. Thermochemical data obtained from alcoholysis of zirconium tetralkyl species show that the mean bond energy of Zr—O is 50 kcal/mole greater than that of Zr—C (40).

The fate of 10 depends on whether or not the zirconium dihydrido species, $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$, is present. In the presence of the dihydride, further reduction occurs to yield the methoxide complex (7). In the absence of the dihydride, 10 undergoes a dimerization reaction, yielding 11:



The possible mechanism suggested by Bercaw for these processes is



Scheme 1

shown in Scheme 1 (37). For clarity, the pentamethylcyclopentadiene ligands have been omitted.

This reaction is significant in terms of Fischer-Tropsch chemistry, because it represents the first well-characterized system in which a coordinated carbonyl is reduced by molecular hydrogen. Furthermore, complex 11 could be viewed as a precursor to ethylene glycol which, as previously indicated, is a highly desirable product from the reaction between carbon monoxide and hydrogen.

In a closely related system, Huffmann *et al.* have reported that when a toluene solution of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$ is treated with a mixture of hydrogen and carbon monoxide at 150°C, methane, but no methanol, is produced (41).

When deuterium is used in place of hydrogen, CD_4 is produced; however, the methanation is not catalytic in titanium and only the CO's originally present on the titanium are reduced. After the reaction, a blue crystalline complex was isolated; it was shown, by X-ray crystallography, to be a regular octahedral cluster of formula $(\eta^5\text{-C}_5\text{H}_5)_8\text{Ti}_6\text{O}_8$ containing symmetrical face-bridging oxygen atoms. The favorable thermodynamics of methanation are dependent on the formation of water (4), and it is suggested that this water, or a protic precursor to it, is responsible for the formation of the $(\eta^5\text{-C}_5\text{H}_5)_8\text{Ti}_6\text{O}_8$ complex. As proposed for the zir-

conium system (37), metal-oxygen bonding, in either a π -formyl (12) or a 1,2- $(\mu_2\text{-CH}_n\text{O})$ structure (13, $n = 0, 1, 2$), is thought to be an important mechanistic factor in this reduction.



(12)



(13)

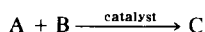
A common feature in the acyl/CO reductions outlined above is activation of the carbonyl by oxygen coordination. It seems likely that this type of activation also played an important role in the first published report of catalytic reductive polymerization of CO at room temperature (42). Here, Schwartz and Shoer showed that, with $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$ as catalyst, $i\text{-Bu}_2\text{AlH}$ will reduce CO at room temperature and 1–4 bar to give, on hydrolysis, a mixture of linear aliphatic alcohols. Thus, addition of CO to a mixture of $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$ and $i\text{-Bu}_2\text{AlH}$ yields an oily product which, on hydrolysis with $\text{H}_2\text{O}/\text{H}_2\text{SO}_4$, gives methanol, ethanol, 1-propanol, and 1-butanol in the molar ratio 1.00:0.12:0.15:0.03. Use of ^{13}CO established that these linear alcohols were derived from CO by incorporating CO into each carbon unit of the alkyl chain.

Although the mechanistic details of this system are not yet clear, it certainly represents a significant step toward the design of Fischer-Tropsch catalysts capable of functioning under mild conditions of temperature and pressure. Furthermore, it lends some credence (*vide infra*) to the suggestion that multimetal systems may be more useful than monometallic systems for the reductive polymerization of CO.

C. Homogeneous Catalysts for the Fischer-Tropsch and the Water Gas Shift Reactions

1. Homogeneous Fischer-Tropsch Catalysts

The problem of coreacting carbon monoxide and hydrogen to give products is, in essence, one of designing a catalytic system which can activate both these molecules in such a way that they easily combine. This rather obvious statement of the problem applies to all catalytic systems of the type



and forms the basis for any attempt at catalyst design. If we consider

catalysis—homogeneous or heterogeneous—in terms of molecule activation, then we can distinguish two basic activation processes:

1. Activation by coordination, in which a substrate XY interacts with a metal center in such a way that the integrity of XY is maintained. In such a process, although the distribution of electrons over the XY bond(s) may be radically altered, X and Y remain formally bonded to each other, and in any exchange process XY in its entirety is exchanged rather than either X or Y individually. Examples in homogeneous systems would be coordination of carbon monoxide or ethene at single metal centers; the corresponding process in heterogeneous catalysis would be “nondissociative adsorption.”

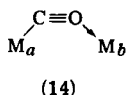
2. Activation by addition, in which a substrate XY interacts with a metal center in such a way that the integrity of XY is destroyed, i.e., the bond(s) holding XY together is (are) formally broken. In homogeneous systems such a process generally falls under the heading “oxidative addition,” and there are several reviews in which the importance of such oxidative addition reactions in homogeneous catalysis have been discussed (43–48). Addition of hydrogen to a metal center to give a dihydride is one well-studied example of this type of activation (49). The corresponding process in heterogeneous catalysis would be “dissociative adsorption.”

If we now consider the CO/H₂ system, then the catalytic process can be envisaged as a combination of (1) and (2) above, carbon monoxide being activated by coordination and hydrogen by addition. If we adopt the view that in a transition metal hydride the hydrogen is present as an anionic hydride ligand (:H[−]) (49) then, given the charge separation



in carbon monoxide, initial addition could be pictured as involving hydride attack at the carbonyl carbon. In order to facilitate such an attack, we must make the hydride as electron-rich and the carbonyl carbon as electron-poor as possible. Furthermore, if we accept the thermodynamic objection previously proposed to a “simple” metal formyl complex, we should aim for a system in which *both* the carbonyl oxygen and the carbonyl carbon interact with a metal center. The highly hydridic nature of the Zr—H has been suggested to be important in its reaction with Zr—CO unit (37). In both the BH₃ reduction of coordinated acyl (32) and the *i*-Bu₂AlH reduction of carbon monoxide (42), the Lewis acidity of the reductant is thought to play a significant role.

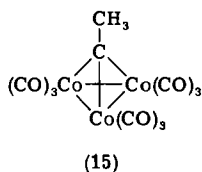
The idea (50, 51) of dual coordination of CO implies the presence of two coordination centers in a Fischer-Tropsch catalyst system, i.e., a carbonyl carbon coordinating center, M_a , and a carbonyl oxygen coordinating center, M_b (14). It is this concept which has led at least two groups to examine transition metal carbonyl cluster compounds as homogeneous Fischer-Tropsch catalysts.



Four simple (i.e., containing only carbonyl ligands) transition metal cluster compounds, viz. $\text{Ru}_3(\text{CO})_{12}$ (52), $\text{Os}_3(\text{CO})_{12}$ (52, 53), $\text{Ir}_4(\text{CO})_{12}$ (52, 53), and $\text{Rh}_6(\text{CO})_{16}$ (54), have been reported to catalyze the formation of hydrocarbon products from carbon monoxide and hydrogen. The rhodium cluster, which preferentially catalyzes the formation of oxygen-containing products, is dealt with in Section II,C,2. Of the remaining three complexes, $\text{Os}_3(\text{CO})_{12}$ and $\text{Ir}_4(\text{CO})_{12}$ have been found to catalyze the hydrogen reduction of carbon monoxide to methane under very mild conditions (140°C, CO/H_2 2 bar) (53). Reaction rates under these mild conditions are low (~1% conversion in 3–5 days with 3–5 catalyst turnovers) (53); however, under more stringent conditions (300°C, 100 bar, CO/H_2 1:1), somewhat higher rates were observed, and using $\text{Os}_3(\text{CO})_{12}$ hydrocarbon products up to C_{30} were detected (52). Under these conditions $\text{Ru}_3(\text{CO})_{12}$ was found to be more effective than either $\text{Os}_3(\text{CO})_{12}$ or $\text{Ir}_4(\text{CO})_{12}$ for the production of linear alkanes from mixtures of carbon monoxide and hydrogen. The order of activity is $\text{Ru} > \text{Os} > \text{Ir}$, with $\text{Ru}_3(\text{CO})_{12}$ being about three times as active as the corresponding osmium system (52). In a typical batch experiment with $\text{Ru}_3(\text{CO})_{12}$ in heptane, 2.5 g of linear alkanes in the range C_3 – C_{30} were produced per g ruthenium over a reaction time of 5 hours (temp. 300°C, initial pressure at 25°C 100 bar, CO/H_2 1:1). The selectivity to linear alkane formation is greater than 90%. At no stage in the reaction was metallic ruthenium detected.² Examination of the liquid phase recovered after the reaction showed that the metal carbonyl cluster compound had broken down during the reaction to give the mononuclear species, $\text{Ru}(\text{CO})_5$. With $\text{Os}_3(\text{CO})_{12}$, $\text{H}_2\text{Os}(\text{CO})_4$ was detected after the reactions. These mononuclear carbonyl species were found to be inactive as homogeneous Fischer-Tropsch catalysts. Similarly, monomeric cobalt carbonyl species, which have long

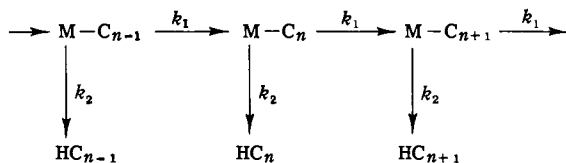
² Only visual inspection of the reaction solution was made. Since the metals used, i.e., Ru, Os, Ir, Co, are heterogeneous Fischer-Tropsch catalysts, definite proof of the homogeneity of these systems must await detailed spectroscopic and kinetic measurements.

been known as active hydroformylation catalysts (55), show no appreciable activity in the synthesis of hydrocarbons from CO and H₂ mixtures. However, the cobalt cluster compound **15** (56), although rapidly deactivated under the reaction conditions (300°C, 100 bar, CO/H₂ 1:1), showed some initial activity for the production of linear alkanes from CO and H₂ (yield $\sum_{n=3}^{23} \text{HC}_n \text{ g/g metal} = 3.6$, where HC_{*n*} are linear alkanes with carbon number *n*) (57).



These observations, coupled with the findings of Muetterties *et al.* that none of a large number of mononuclear coordination catalysts examined showed any activity for the H₂/CO reaction (53), lend further support to the idea that more than one metal center is necessary for the catalytic formation of hydrocarbon products from synthesis gas.

With the Ru₃(CO)₁₂ and Os₃(CO)₁₂ catalyst systems it is possible, by determining the relative amounts of alkane products in the range C₁₀–C₂₆ and assuming the simple kinetic picture



(where HC_{*n*} presents a linear alkane with *n* carbon atoms), to estimate the ratio k_1/k_2 , where k_1 is related to the overall rate constant of propagation and k_2 to that of termination. Under steady-state conditions, with the assumptions that k_1 and k_2 are independent of chain length (*n*) over the range studied and that the termination step is irreversible [i.e., once the alkane (HC_{*n*}) has left the metal catalyst it does not return to give rise to a metal-alkyl intermediate (M–C_{*n*})], the concentration of alkane products decreases according to a geometric progression:

$$[\text{HC}_n] = ar^{n-1}$$

where *r*, the progression coefficient, is equal to $k_1/(k_1 + k_2)$. Thus a plot of log[HC_{*n*}] against (*n* – 1) is linear and from the gradient, log *r*, the ratio k_1/k_2 can be obtained. A typical plot for Ru₃(CO)₁₂ in heptane is shown in Fig. 2. Although this plot only covers the range C₁₀–C₂₅, rea-

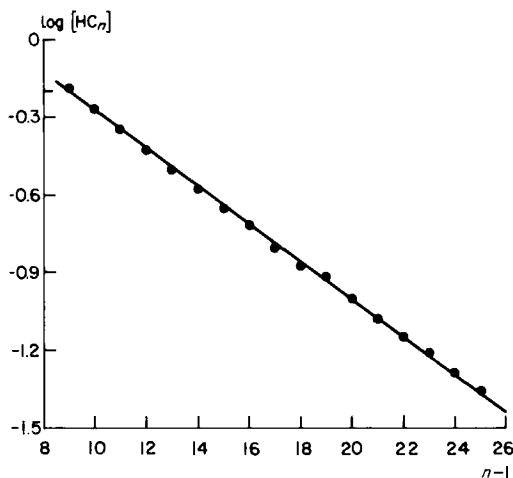


FIG. 2. Logarithm of the linear alkane, HC_n , concentration as a function of carbon chain length, n .

sonably good linearity has been found over the range C_8 – C_{30} (57). Above C_{30} , the experimental points generally lie below the line, and in most cases the values for C_1 and C_2 are too high. Similar results have been obtained with heterogeneous catalysts operating under steady-state conditions (7).

The value of k_1/k_2 is diagnostic of the reaction. A very small value, e.g., 10^{-2} , indicates that $k_2 \gg k_1$ and that the reaction gives essentially gaseous products. A large value, e.g., 100, indicates the reverse, viz., $k_2 \ll k_1$, resulting in waxlike products. For both the ruthenium and osmium systems, k_1/k_2 is in the range 2–10, implying a relatively small difference between k_1 and k_2 , i.e., a relatively small difference in the overall free energy of activation between the propagation and termination steps. The k_1/k_2 ratio is solvent-dependent for the $\text{Ru}_3(\text{CO})_{12}$ system, ranging from ca. 3 in methanol to ca. 8 in THF. Figure 3 illustrates the effect of k_1/k_2 on the alkane product distribution.

As previously mentioned, both $\text{Os}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$ are converted into inactive mononuclear species under certain Fischer-Tropsch reaction conditions. One way to prevent cluster rupture is to use a "cap" ligand, i.e., a tridentate ligand capable of simultaneously complexing all three metal centers and thus of holding them together (57). Such a ligand could be visualized as a cap fitting over the cluster's head and protecting it; the resulting cluster is then referred to as a "capped complex." An example of such a capped complex is the cobalt cluster $\text{CH}_3\text{CCo}_3(\text{CO})_9$.

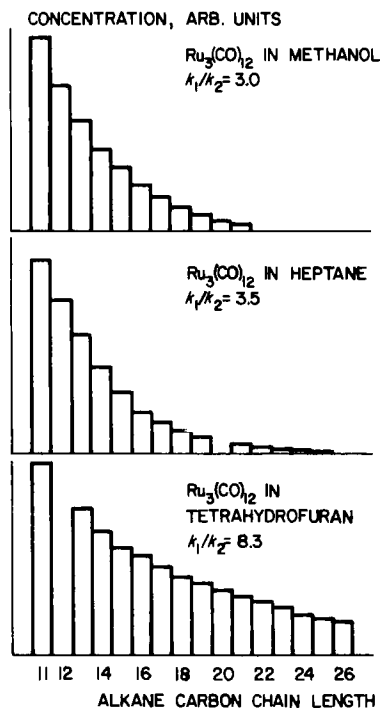
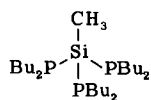


FIG. 3. Linear alkane product distribution as obtained in methanol, heptane, and tetrahydrofuran at 300°C with an initial $\text{CO}/\text{H}_2 = 1/1$ pressure of 100 bar. (Reproducibility of k_1/k_2 figures not better than ± 1 .)

(15). As a cap for $\text{Ru}_3(\text{CO})_{12}$, methyltri-(di-*n*-butylphosphino)-silane (16) was prepared (57).



(16)

Addition of this ligand to $\text{Ru}_3(\text{CO})_{12}$ in refluxing benzene solution gives the capped complex $\text{Ru}_3(\text{CO})_9\{\text{P}(\text{C}_4\text{H}_9)_2\}_3\text{SiCH}_3$, the structure of which is shown in Fig. 4 (58). This complex, when dissolved in *n*-heptane in the presence of carbon monoxide and hydrogen, catalyzes the formation of methane, ethane, propane, and butane at 300°C and ca. 150 bar, CO/H_2 1:1 (57). Although the capped complex was not recovered unchanged after reaction (20 hours at 300°C), no ruthenium pentacarbonyl was detected by infrared analysis.

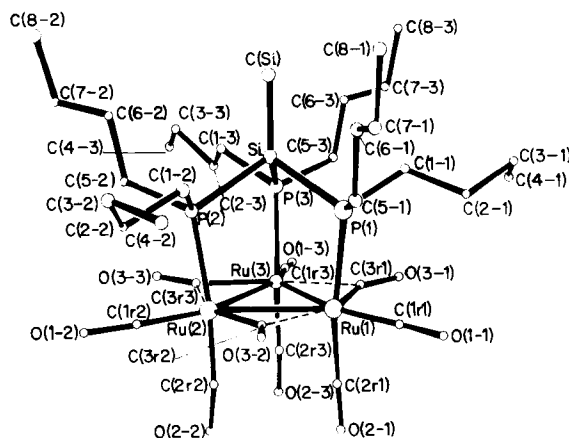


FIG. 4. The molecular structure of the "capped" complex $\text{Ru}_3(\text{CO})_9\{\text{P}(\text{C}_4\text{H}_9)_2\}\text{SiCH}_3$.

Another cluster-modified system which has been reported to catalyze the production of aliphatic hydrocarbons from carbon monoxide and hydrogen is that obtained when $\text{Ir}_4(\text{CO})_{12}$ is dissolved in molten $\text{NaCl} \cdot 2\text{AlCl}_3$ with an $\text{Al}:\text{Ir}$ ratio of 1000:1 (59). This system is considerably more active than simple $\text{Ir}_4(\text{CO})_{12}$, with turnover times of 10–15 minutes (cf. ca. 24 hours) at 180°C and 1–2 bar, CO/H_2 1:3. Of the other carbonyl complexes examined with AlCl_3 , only $\text{Ru}_3(\text{CO})_{12}$, $\text{Rh}_6(\text{CO})_{16}$, and $\text{Rh}_4(\text{CO})_{12}$ showed any appreciable activity. As the rhodium-based system is heterogeneous at 180°C , it is not certain that this particular catalytic reaction occurs in the liquid phase. The $\text{Ir}_4(\text{CO})_{12}$ catalyzed reactions are, on the basis of light-scattering and comparative rate data criteria, thought to be homogeneous.

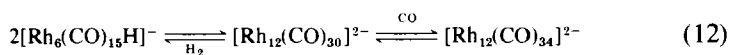
The distribution of hydrocarbon products found with the $\text{Ir}_4(\text{CO})_{12}/\text{AlCl}_3$ system is unusual in that of the four hydrocarbons detected, i.e., methane, ethane, propane, and isobutane, *ethane* is the major product. At the initial stage of the reaction, the ethane-to-methane ratio is 10:1, decreasing to 2:1 after 0.5–3 days. The reason for this variation with reaction time is not clear, although it was felt unlikely that it resulted from ethane being cracked to methane during the course of the reaction (59).

Finding ethane to be the major product is a significant result, because for all the other systems described above, and indeed for Fischer-Tropsch catalysts in general, methane is the major hydrocarbon product. Furthermore, as is discussed in Section III, high selectivity to C_2 could have important mechanistic as well as commercial implications.

2. Syngas to Ethylene Glycol

In economic terms, ethylene glycol is a very desirable product of the reaction between carbon monoxide and hydrogen. The first report of its production directly from syngas using a homogeneous catalyst appeared in 1951, when Gresham of E. I. Du Pont de Nemours and Company claimed that certain cobalt complexes (e.g., cobalt acetate), dissolved in a suitable solvent (e.g., acetic acid), catalyzed the conversion of CO/H₂ mixtures to polyfunctional oxygen-contained organic compounds (60). Ethylene glycol, higher polyhydric alcohols, and esters of these alcohols were the principal products recovered. For this reaction pressures in excess of 1000 bar and temperatures in the range 180°–300°C were required. In a typical experiment, a 2:1 mixture of CO:H₂, when heated under a pressure of 3000 bar at 225°–246°C for 1 hour in the presence of acetic acid containing 0.035 g cobalt acetate per cm³, gave 13.7 g of a mixture of ethylene glycol diacetate and glycerol triacetate. In 1974 Pruett and Walker of Union Carbide Corporation disclosed that under similar high-pressure conditions, ca. 3000 bar CO/H₂, certain soluble rhodium complexes were capable of catalyzing the reaction between carbon monoxide and hydrogen to give as major product (ca. 70%) ethylene glycol (54). Since their original disclosure, a number of patents and *offenlegungsschriften* have appeared covering many aspects of this system (61). Only a brief account of these findings will be given here.

The catalyst precursor generally used for the reaction is rhodium dicarbonyl acetylacetonate. However, detailed infrared studies under the reaction conditions (ca. 1000 bar CO/H₂ and 200°C) have shown both the [Rh(CO)₄]⁻ and the [Rh₁₂(CO)_{34–36}]²⁻ anions to be present in various concentrations at different stages of the reaction (62, 63). It is suggested that rhodium carbonyl clusters, characterized as having three intense infrared absorptions at 1868 ± 10, 1838 ± 10, and 1785 ± 10 cm⁻¹, are responsible for the catalysis (62), and it is believed that the reaction is dependent upon the existence of the following equilibria:



The infrared spectrum of a solution of rhodium dicarbonyl acetylacetonate with either 2-hydroxypyridine or piperidine (4 molar excess over rhodium) in tetraglyme at 210°C under a CO/H₂ pressure of either 714 or 1225 bar contained bands consistent with the existence of the above equilibria [Eq. (12)]. The concentration of [Rh₁₂(CO)₃₄]²⁻ was found to increase as the CO/H₂ pressure was increased. In the absence of either 2-hydroxypyridine or piperidine, a higher pressure (ca. 1700 bar) was

required for the establishment of the equilibria. In the absence of the nitrogen "ligands," the neutral complex $\text{Rh}_6(\text{CO})_{16}$ was detected at 714 bar CO/H_2 .

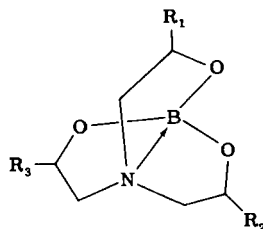
It is suggested that the function of the organic ligands is to provide counterions for the ionic clusters shown in equilibria (12) either by complexing with rhodium carbonyl cluster ions or by ionically associating with the cluster (62). Although organic ligands containing at least one nitrogen atom and/or one oxygen atom have been found to be suitable, simple counterions such as monovalent (e.g., Li^+ , Na^+ , etc.) or polyvalent (e.g., Mg^{2+} , Ca^{2+} , Al^{3+}) metal ions can also be used (62).

A wide range of transition metal complexes have been screened as possible catalysts for the reaction, but so far only systems containing rhodium have been reported to show any appreciable activity for the formation of polyhydric alcohols. With respect to the organic products of the rhodium-catalyzed reaction, methanol and ethylene glycol are the major components, the ratio of the two appearing to depend on the nature of the organic ligand and on the CO/H_2 pressure. At a CO/H_2 (mole ratio 65/35) pressure in the range 1260–1400 bar with 2-hydroxypyridine as ligand (reaction temp. 230°C for 2 hours), the ratio of ethylene glycol to methanol was found to be ca. 7:1; with 3-hydroxypyridine as ligand, under the same conditions of temperature and pressure, the ratio decreased to ca. 2:1. Similarly, decreasing the CO/H_2 pressure from ca. 1300 bar to ca. 650 bar caused a decrease in the ethylene glycol:methanol ratio. The other minor products of the reaction include methyl formate, ethanol, glycerine, and in some cases propylene glycol. Use of inorganic counterions, e.g., Mg^{2+} , Al^{3+} , appears to slightly favor the production of propylene glycol. It is claimed that the process proceeds in the virtual absence of the following methanation reaction: (54).



The system is not limited to the use of synthesis gas as feed. Mixtures of carbon dioxide and hydrogen also give rise to the formation of polyhydric alcohols, and it is also claimed that the reaction mixture can consist of steam and carbon monoxide (62). This latter claim is consistent with the presence of CO_2 in the reaction mixture when CO/H_2 is used as feed [infrared data (62)], and suggests that these ionic rhodium systems are also active catalysts for the water gas-shift reaction (*vide infra*).

One problem apparently associated with the process is the loss of catalyst during the reaction. It is suggested that rhodium losses may be significantly reduced when the reaction is conducted in the presence of a trialkonolamine borate, $\text{B}(\text{OR})_3\text{N}$ (63). Borates of type 17, where R_1 , R_2 , $\text{R}_3 = \text{H}$ or Me , were found to be particularly effective.



(17)

It is thought that these trialkanolamine borates may enhance the reactivity of the rhodium carbonyl anions by minimizing their tendency to form "contact ion pairs" in solution under the reaction conditions employed. The same patent discloses that ammonium salts and salts of Groups I and II, especially cesium and ammonium carboxylate salts, function as promoters (63).

Rhodium losses can also be reduced by using a two-phase system to separate the polyol products from the catalyst solution (64). In this modification the reaction is carried out in a "production" solvent (e.g., tetraglyme). In order to separate the products, water and an essentially water-immiscible organic extraction solvent (e.g., dichloromethane or chloroform) are added. The resulting two-phase system then consists of a water phase containing the alcohol products and an organic phase containing essentially all the rhodium complex.

Although in most of the reactions described above the multimetallic rhodium anions are prepared *in situ* from, for example, $\text{Rh}(\text{CO})_2(\text{acac})$, they can also be introduced as such into the reaction medium. Three patents have appeared detailing the preparation of $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ salts with monovalent {e.g., Cu^+ , Ag^+ , $[\text{Rh}(\text{CO})_2(2,2'\text{-bipyridine})]^+$, $[\text{Ir}(\text{CO})_3(\text{pyridine})]^+$ } (65), divalent [e.g., Mg^{2+} , Ca^{2+} , Be^{2+} , Sr^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+}] (66), and trivalent (e.g., Al^{3+} , Ga^{3+} , Ir^{3+} , Se^{3+} , Re^{3+} , Y^{3+}) (67) cations.

In addition to these homometallic (rhodium) clusters, several heterometallic clusters of the type $[\text{M}_x\text{M}_{12-x}^{1-}(\text{CO})_{30}]^{2-}$, where M and M^1 are each different metals selected from the Co, Rh, Ir triad ($x = 1-11$), have been described and claimed to be useful catalysts in the reaction between carbon monoxide and hydrogen to produce oxygenated products (68, 69). These complexes can be prepared from the heterometallic dodecacarbonyl complexes, $[\text{M}_y\text{M}_{4-y}^{1-}(\text{CO})_{12}]$ (M, $\text{M}^1 = \text{Co}$, Rh, or Ir; $y = 1-3$), by simply mixing the appropriate dodecacarbonyl species in THF under nitrogen and then adding water (70). They can be isolated by adding a suitable cation e.g., Al^{3+} , Mg^{2+} , Ca^{2+} , etc.

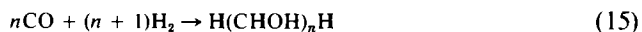
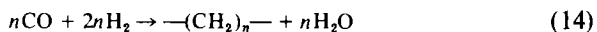
Although it is clear that Union Carbide has put a considerable research

effort into this process, there have been, as yet, no announcements, of plans to go into commercial operation using these homogeneous rhodium catalysts. However, in a recent article (71), the president of Chem Systems expressed the belief that this technology is likely to be commercialized in the late 1980's and that its economics will be viable, relative to existing, ethylene-based processes.

In all the homogeneous catalysis systems described in Sections II,C,1 and II,C,2, the active catalyst, or at least the catalyst precursor, is a complex containing three or more metal centers. Up to the present time no definitive evidence supporting cluster catalysis has been reported, but then nor are there any reports of mononuclear complexes which catalyze the reductive polymerization of carbon monoxide. This lends some weight to the speculative suggestion, discussed by Muetterties (50), that for CO hydrogenation more than one coordination site is needed. Although with heterogeneous catalysts accurate descriptions of the active site are difficult, Bond and Turnham have suggested (72), on the basis of some studies of CO hydrogenation over Ru—Cu/SiO₂ catalyst, that the active site for the reaction on pure ruthenium is an ensemble of about four Ru atoms. Similar studies of CO hydrogenation over heterogeneous Ni/Cu catalysts have led Araki and Ponc to suggest that more than one nickel center is involved in the active site for CO dissociation (73).

3. Homogeneous Shift Catalysts

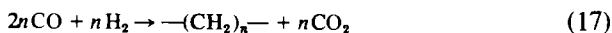
Because the synthesis gas produced from coal is generally relatively poor in hydrogen, a typical CO:H₂ ratio being ca. 1:1, and because, as can be seen from Eqs. (14) and (15), a hydrogen-rich gas is required for the production of hydrocarbons and chemicals, a hydrogen enrichment step is usually necessary for the Fischer-Tropsch process.



One method of increasing the hydrogen content of synthesis gas is via the water gas-shift reaction [Eq. (16)]:



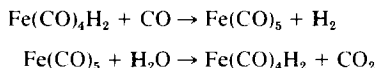
A Fischer-Tropsch catalyst system capable of linking reactions (14) and (16), i.e., a synthesis catalyst having appreciable shift activity, would clearly be of considerable interest in that it would allow the use of hydrogen-poor synthesis gas for the production of hydrocarbons via the following overall reaction:



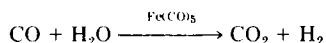
The data available for heterogeneous Fischer-Tropsch catalysts indicate that with cobalt-based catalysts the rate of the water gas-shift reaction is very slow under the synthesis conditions (5). Thus, water is formed together with the hydrocarbon products [Eq. (14)]. The iron-based catalysts show some shift activity, but even with these catalysts, considerable quantities of water are produced.

With reference to the homogeneous catalyst systems thus far reported for the synthesis of hydrocarbons/chemicals from carbon monoxide and hydrogen, only the anionic rhodium systems of Union Carbide show any appreciable shift activity. With neutral species of the type $M_3(CO)_x$ ($M = Ru$ or Os), only small quantities of carbon dioxide are produced under the synthesis conditions (57).

There have been several reports of homogeneous systems which catalyze the shift reaction in the absence of the synthesis reaction. Probably the first example of such a system was that reported by Reppe and Reindl in 1953 based on iron pentacarbonyl (74). They suggested that in the presence of a suitable base the following catalytic cycle could be established:



i.e.,

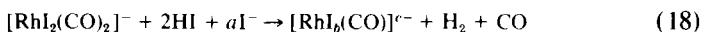


However, since the goal of this work was the synthesis of alcohols from olefins via hydrohydroxymethylation (75, 76), little attention was given to developing a shift-catalyst per se. Pettit has recently reexamined some of this work and shown that, by careful control of the pH of the reaction mixture, systems based on either $Fe(CO)_5$ or $Cr(CO)_6$ can be developed for the production of either formic acid or methanol from carbon monoxide and water (77, 78). Each of these latter systems involves the formation of metal hydride complexes; consequently, molecular hydrogen is also produced according to the shift reaction [Eq. (16)].

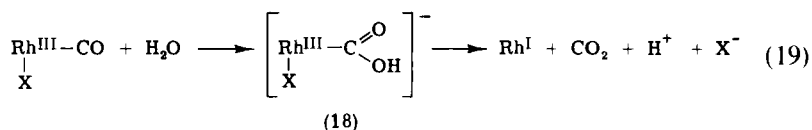
In 1977 Ford and co-workers showed that $Ru_3(CO)_{12}$ in the presence of a ca. fiftyfold excess of KOH catalyzes the shift reaction at 100°C/1 bar CO (79). The effectiveness of the system increased markedly as temperature was increased (rate of hydrogen formation approximately quadrupled on raising the temperature from 100° to 110°C), and over a 30-day period catalyst turnovers of 150 and 3 were found for $Ru_3(CO)_{12}$ and KOH, respectively. Neither methane nor methanol was detected in the reaction products. Although the nature of the active ruthenium species could not be unambiguously established, infrared data indicated that it is not $Ru_3(CO)_{12}$, and the complexity of the infrared spectrum in the

carbonyl stretching region suggested the presence of polynuclear anionic and/or hydridic carbonyl complexes.

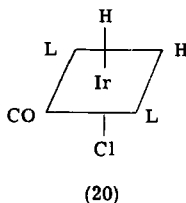
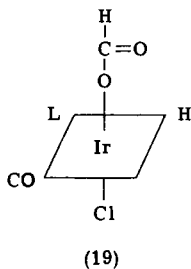
In addition to the polymeric rhodium catalysts previously discussed, monomeric rhodium systems prepared from $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ by addition of strong acid (HCl or HBF_4) and NaI in glacial acetic acid have also been shown to be active homogeneous shift catalysts (80). The active species is thought to be an anionic iodorhodium carbonyl species, dihydrogen being produced by the reduction of protons with concomitant oxidation of $\text{Rh}(\text{I})$ to $\text{Rh}(\text{III})$ [Eq. (18)], and carbon dioxide by nucleophilic attack of water on a $\text{Rh}(\text{III})$ -coordinated carbonyl [Eq. (19)].



$$(a = 0, 1; b = 4, 5; c = 1, 2)$$



In an alternative sequence suggested by Eisenberg *et al.* (80), X in Eq. (19) is hydride. CO_2 production then proceeds via β -elimination from the oxygen OH in **18**, giving a rhodium(III) dihydrido species which can then reductively eliminate H_2 . Some support for this latter suggestion is provided by the observation that iridium(III) species of type **19**, formed by oxidative addition of formic acid to *trans*- $[\text{IrCl}(\text{CO})\text{L}_2]$ (L = tertiary phosphine), rapidly lose CO_2 to give the dihydrido species **20** (81).



Formally, at least, there is some mechanistic similarity between the water gas-shift and the Fischer-Tropsch reactions in that both can be considered in terms of an initial nucleophilic attack at the carbon atom of a coordinated carbon monoxide, OH^- or H_2O being the nucleophile in the gas-shift reaction and H^- that in the Fischer-Tropsch reaction.

Even outside the context of the Fischer-Tropsch synthesis, the water gas-shift reaction has considerable commercial importance. In addition to being used to increase the hydrogen content of synthesis gas, it is

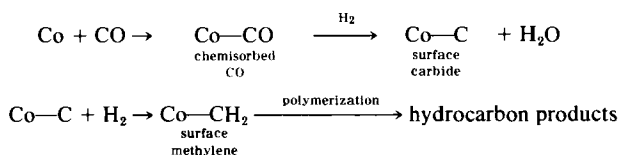
widely used to remove carbon monoxide from the N_2/H_2 feed for ammonia synthesis (82). On an industrial scale, the shift reaction is carried out with heterogeneous iron- or copper-based catalysts at temperatures above ca. 200°C (83). However, hydrogen formation via the shift equilibrium [Eq. (16)] is favored by low temperatures (80). The high temperatures used industrially are dictated by kinetic considerations, i.e., low catalyst activity at below ca. 220°C . Thus, the development of more active catalyst systems is presently an area of considerable interest.

III

POSSIBLE MECHANISMS FOR THE FISCHER-TROPSCH REACTION

The mechanisms proposed over the last 50 years for the Fischer-Tropsch synthesis, principally on the basis of studies using heterogeneous catalyst systems, may be divided into three main classes: (a) metal-carbide mechanisms; (b) hydroxyl "carbene," $=\text{CH}(\text{OH})$, condensation mechanisms; and (c) CO insertion mechanisms.

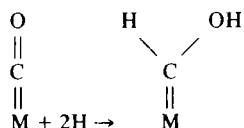
The earliest theory, advanced by Fischer and Tropsch in 1926 (84), proposed that the reaction proceeded via formation of intermediate metal carbides which react on the catalyst surface to form methylene groups. It was then suggested that these methylene groups polymerize on the surface to form hydrocarbon chains, which desorb as saturated and unsaturated hydrocarbons. In 1939 Craxford and Rideal expanded the carbide theory, proposing (85), for cobalt-based catalysts, the following reaction sequence:



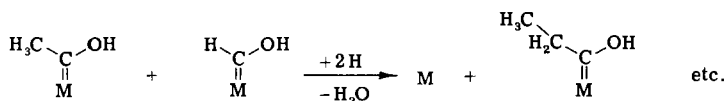
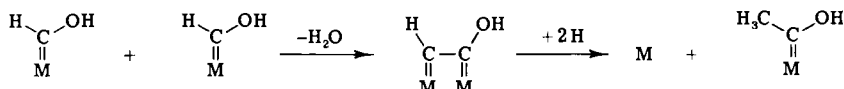
Subsequent studies have failed to support the carbide theory, and it is now generally accepted that carbides of the type proposed by Craxford play little or no part in the Fischer-Tropsch synthesis (86, 87). It has, however, recently been suggested, by analogy with the mechanism proposed for the Haber synthesis of ammonia, that carbides formed by dissociative absorption of carbon monoxide would be expected to be readily hydrogenated and could therefore be of importance in Fischer-Tropsch synthesis over heterogeneous catalyst (88).

A second theory for the mechanism, proposed by Storch *et al.* in 1951

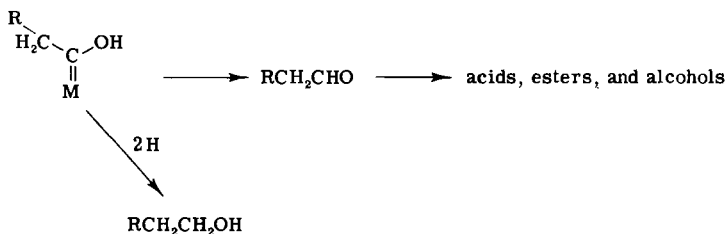
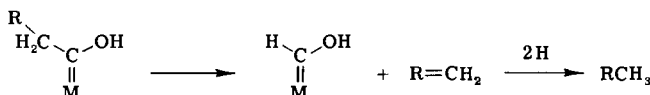
(4), suggested the formation of =CH(OH) groups on the catalyst surface via hydrogenation of chemisorbed carbon monoxide:



Chain growth is then thought to occur via condensation of these groups with elimination of water and addition of hydrogen:



and termination via one of the sequences shown below:

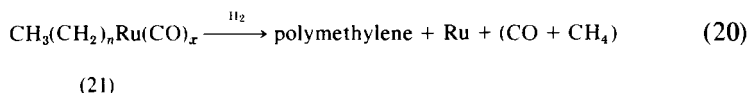


This mechanism differs from the "carbide" theory in that chain growth involves oxygen-containing groups and is thought to take place on the ultimate or penultimate carbon atoms of the longest chain by surface condensation reactions.

The third class of mechanisms is that originated by Pichler and Schulz in which chain growth is accomplished by direct insertion of an absorbed CO molecule into a carbon-metal bond produced by hydrogenation of a surface carbonyl (89). A complete representation of this mechanism (see

89) explains all the various types of products found in the Fischer-Tropsch synthesis, and in Scheme 2 only that part leading to hydrocarbon products is shown.

The mechanism of Pichler *et al.* incorporates many concepts which have now been experimentally demonstrated in organometallic chemistry, and it is interesting to note that as early as 1947 Pichler had suggested that metal carbonyl species might well play an important role in the reaction (16). Furthermore, in his mechanistic sequence (see Scheme 2), the idea of dual (i.e., carbon and oxygen) coordination, is clearly expounded. In later years he and his co-workers succeeded in isolating alkyl ruthenium carbonyl species of type **21** from the reaction between carbon monoxide and hydrogen in the presence of a heterogeneous ruthenium catalyst at 120°C, 1000 bar CO/H₂ (90, 91). Hydrogenation of these species at slightly higher temperature, 160°C, resulted in the following reaction:

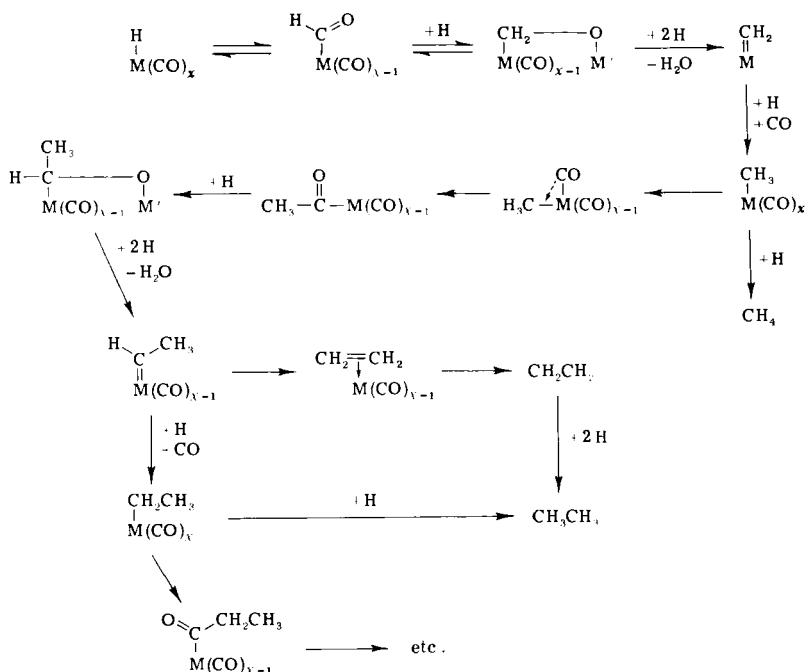


According to Pichler *et al.*, species such as **21** can be seen as intermediates in the high-pressure polymethylene synthesis (91).

Since Pichler's original suggestion, several other mechanisms have been proposed (7, 10); however, in essence these closely resemble that of Pichler. In the subsequent discussion of a possible mechanism for the homogeneous Fischer-Tropsch catalyst systems, many of Pichler's ideas are incorporated.

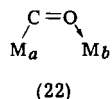
As previously stated in Section I, the Fischer-Tropsch synthesis may be regarded as a reductive polymerization of carbon monoxide. As such, any mechanistic proposal may be divided into three main parts, viz., initiation, propagation, and termination. With reference to initiation, i.e., the formation of a C₁ fragment containing the elements carbon, hydrogen, and, if we disregard the possibility of dissociative interaction of CO in homogeneous systems,³ oxygen, there is a growing quantity of evidence, albeit circumstantial, to suggest that CO coordination via only the carbon atom is insufficient to activate it toward hydrogen reduction. In agreement with Muetterties (50, 51, 53, 59), we would suggest that dual co-

³ Although in heterogeneous systems it has been suggested that interaction of carbon monoxide with the catalyst surface may result in rupture of the CO bond to give absorbed C and O fragments which then undergo further reaction (88), such a reaction is unprecedented in homogeneous systems and at the present time there seems no valid reason to invoke it.



Scheme 2

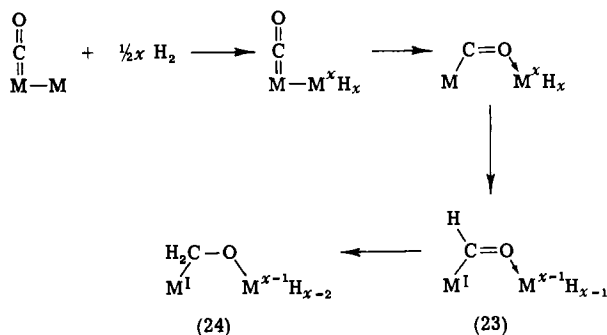
ordination, i.e., at both the carbonyl carbon and the carbonyl oxygen in an intermediate schematically represented as **22**, is necessary.



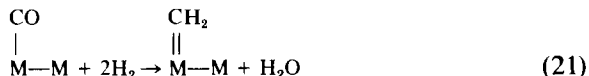
M_b should be an electron-poor center capable of accepting electron density from the carbonyl carbon; i.e., it should be capable of functioning as a Lewis acid. The recent report of Muetterties and Demitras of the promoting effect of aluminum halides on the activity of the $\text{Ir}_4(\text{CO})_{12}$ catalysts lends some support to this suggestion (59). Such Lewis acids suffer from the practical limitation that they are rapidly deactivated by water produced in the Fischer-Tropsch synthesis and, as described in Section II,C,1, $\text{Ru}_3(\text{CO})_{12}$ will, even in the absence of added Lewis acid, catalyze the formation of hydrocarbons from synthesis gas. We would tentatively suggest two possible ways in which carbonyl oxygen-complexing sites may be generated in this latter system.

First, selective oxidation of one of the metal sites in the cluster catalyst,

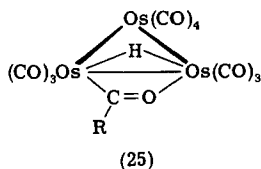
via, e.g., the oxidative addition of molecular hydrogen, could create an electron-poor site in the cluster capable of interacting with carbonyl oxygen. In this case initiation could be envisaged as



where $x = 2$, or possibly 4. Further hydrogenation of the bidentate metal formyl species (23) via, e.g., a species such as 24 analogous to that suggested by Pichler and Schulz (89), could then yield a metal carbene species together with water, the overall process being as follows:



The type of dual carbonyl coordination implicit in 23 is thought to occur in the complex (25) formed when $\text{Os}_3(\text{CO})_{12}$ reacts with various aldehydes, $\text{R}(\text{CO})\text{H}$, where $\text{R} = \text{Ph}$, PhCH_2 , $n\text{-C}_5\text{H}_{11}$, $n\text{-C}_6\text{H}_{13}$, or Pr^i , at ca. 140°C (92).

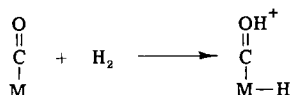


The corresponding reaction with formaldehyde gave $\text{HOs}_3(\text{OMe})(\text{CO})_{10}$, and this is thought to occur via the bridged formyl compound, $\text{R} = \text{H}$.

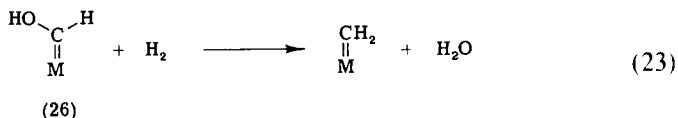
An alternative way in which an electron-poor site could be created would be via the heterolytic splitting of molecular hydrogen i.e.,



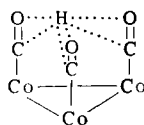
such that the proton, seen as the electron-poor site, immediately becomes coordinated to the carbonyl oxygen:



Such a "protonated" carbonyl should be more susceptible to nucleophilic hydride attack to give **26**. Repetition of the process could then yield a metal carbene species and water:



the net result being the same as that shown in Eq. (21). In the context of the second proposal, it has been reported that the "hydride" ligands in $[\text{Ru}_6\text{H}(\text{CO})_{18}]^-$ (**93**) and $[\text{Co}_6\text{H}(\text{CO})_{15}]^-$ (**94**) give rise to hydrogen signals at very low field, viz., 16.41 and 23.2 ppm in their ^1H NMR spectra; this is possibly indicative of considerable protonic character [cf. 14.68 ppm for the carbonyl oxygen hydrogen in protonated acetone (**95**)]. Chini has suggested that in $[\text{Co}_6\text{H}(\text{CO})_{15}]^-$ the hydrogen is located among the carbonyl ligands, as shown in **27**, rather than on the metal atom(s) (**94**). Clearly, such an interaction would only be feasible in polynuclear carbonyl cluster compounds, and it is perhaps significant that it is this class of complexes which has been found to function as homogeneous Fischer-Tropsch catalysts.

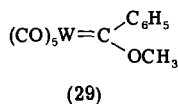
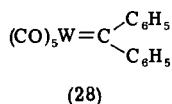


(27)

In essence, these two initiation processes are similar in that they both involve a carbonyl-oxygen interaction with an electron-deficient site and in both cases give rise, after loss of water, to a primary carbene species. They differ as to the position of first H attack on the coordinated carbon monoxide and as to the nature of the first intermediate "CHO" species. In the first case attack is via hydridic hydrogen at the carbonyl carbon to give an aldehydic complex (**23**) which undergoes further reduction via hydride addition at carbonyl carbon, i.e., the route proposed by Pichler and Schulz (**89**). In the second case initial attack is by protonic hydrogen at carbonyl oxygen, followed by hydridic attack at carbonyl carbon, to give an intermediate analogous to that proposed by Anderson *et al.* (**4**). With homogeneous catalyst systems it is difficult to decide, on the basis

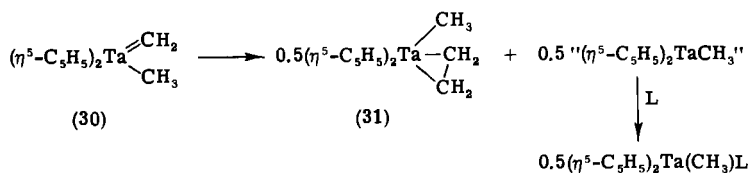
of the evidence presently available, which (if indeed either) of these routes is most probable. With heterogeneous catalysts a similar situation exists, although Kölbel and Hanus have claimed (96), on the basis of detailed product analysis, that with cesium-promoted iron catalysts the primary CHO complex is enolic rather than aldehydic.

In both the initiation processes suggested above, the ultimate C_1 product is a primary carbene species. In the mechanism proposed by Pichler and Schulz (Scheme 2), this species undergoes hydrogenation to give a metal-methyl which can either be further hydrogenated to give methane (termination) or undergo carbonyl insertion to give an acyl complex (propagation). Both these latter reactions are well documented in homogeneous systems, and Casey and Neumann have recently demonstrated the hydrogenation of a carbene fragment to an alkyl unit in complexes of the type **28** and **29** (96a).

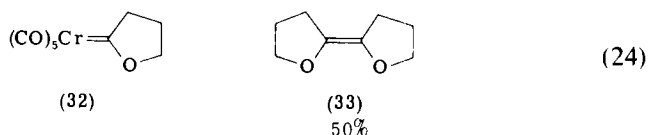


Thus, treatment of **28** with H_2 (69 bar) for 20 hours at 100°C in decalin gave diphenylmethane (41%) together with small amounts of tetraphenylethene and tetraphenylethane. With **29**, under somewhat milder conditions (H_2 , 1.8 bar, 140°C for 5 hours), a 92% yield of benzyl methyl ether was obtained.

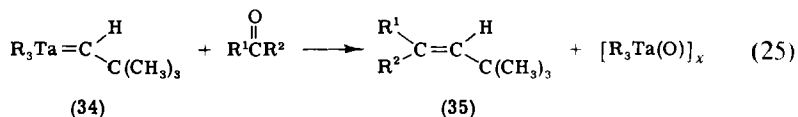
The results obtained with the $\text{Ir}_4(\text{CO})_{12}/\text{NaCl}\cdot 2\text{AlCl}_3$ system, in which ethane is the primary reaction product (59), suggest two other ways in which such a carbene species might react. Given that two such species could be formed in close proximity to each other, e.g., in a metal cluster complex, then dimerization could give ethylene, which in the presence of hydrogen and a transition metal catalyst at $130^\circ\text{--}160^\circ\text{C}$ would be reduced to ethane. There are several reports of transition metal-bonded carbene dimerization reactions: Schrock has shown that $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_3)(\text{CH}_2)$ (**30**), the only known example of a primary (i.e., CH_2) carbene complex, decomposes in C_6D_6 at 25°C to give a ca. 50% yield of **31**, i.e., a complex containing coordinated ethylene (97).



where L can be, e.g., CO or C₂H₄. Casey has reported that the stabilized carbene complex (32) undergoes thermal decomposition with formation of the olefin 33 (98):

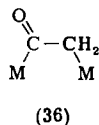


An alternative mode of reaction for a carbene intermediate is suggested by Schrock's work (97, 99). He has demonstrated that the carbene ligands in 30 and in the related species 34, in which R = CH₂C(CH₃)₃, behave as nucleophiles. Thus 34, where R = CH₂C(CH₃)₃, readily reacts with ketones, giving alkenes of type 35 in high yield (99):

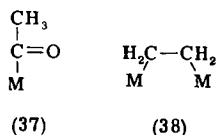


where R¹ = H; R² = Ph, (CH₃)₂N, C₂H₅O; R¹ = CH₃; R² = CH₃, *meta*-tolyl, C₂H₅O.

If the primary carbene proposed as an intermediate in the Fischer-Tropsch synthesis may be viewed as nucleophilic, then an alternative mode of reaction could be attack at the carbonyl carbon of an adjacent carbonyl group to give a C₂ unit of type 36:



Further reduction could then yield either a metal acyl species, 37, or a bridged alkyl species, 38.

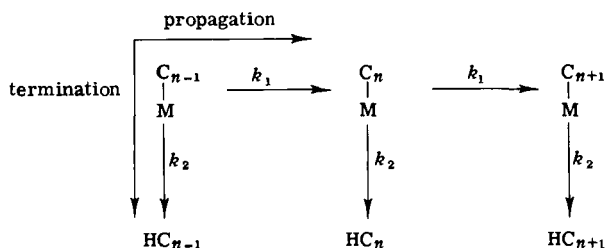


Addition of hydrogen to (37) could give a metal ethyl species, leading to propagation. Addition of hydrogen to (38) could yield either ethane (i.e., termination) or an ethyl-hydrido species which could then participate in a propagation sequence. There are innumerable examples of complexes

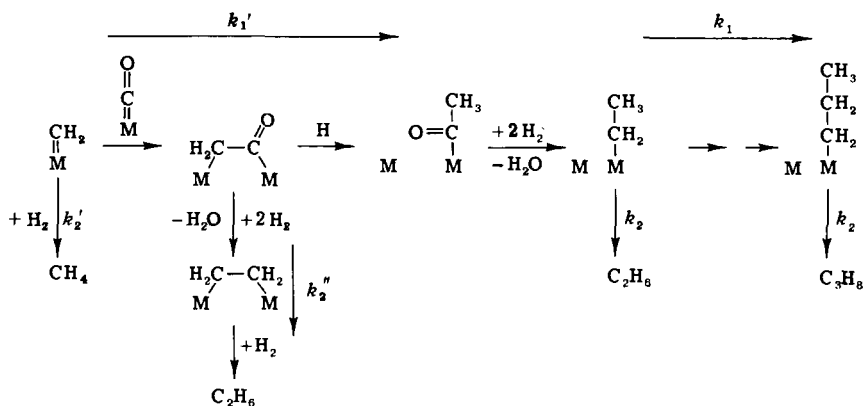
containing acyl groups (28), and recently Beck and Olgemöller have demonstrated the type of bridging suggested in **38** (100).

The existence of such a growth step is consistent with the high proportion of C_2 products found in the $Ir_4(CO)_{12}/NaCl \cdot 2AlCl_3$ system (59). Furthermore, in systems where dimerization is less favored, hydrogenation of the primary carbene fragment could explain the considerable amounts of methane formed in many heterogeneous Fischer-Tropsch systems.

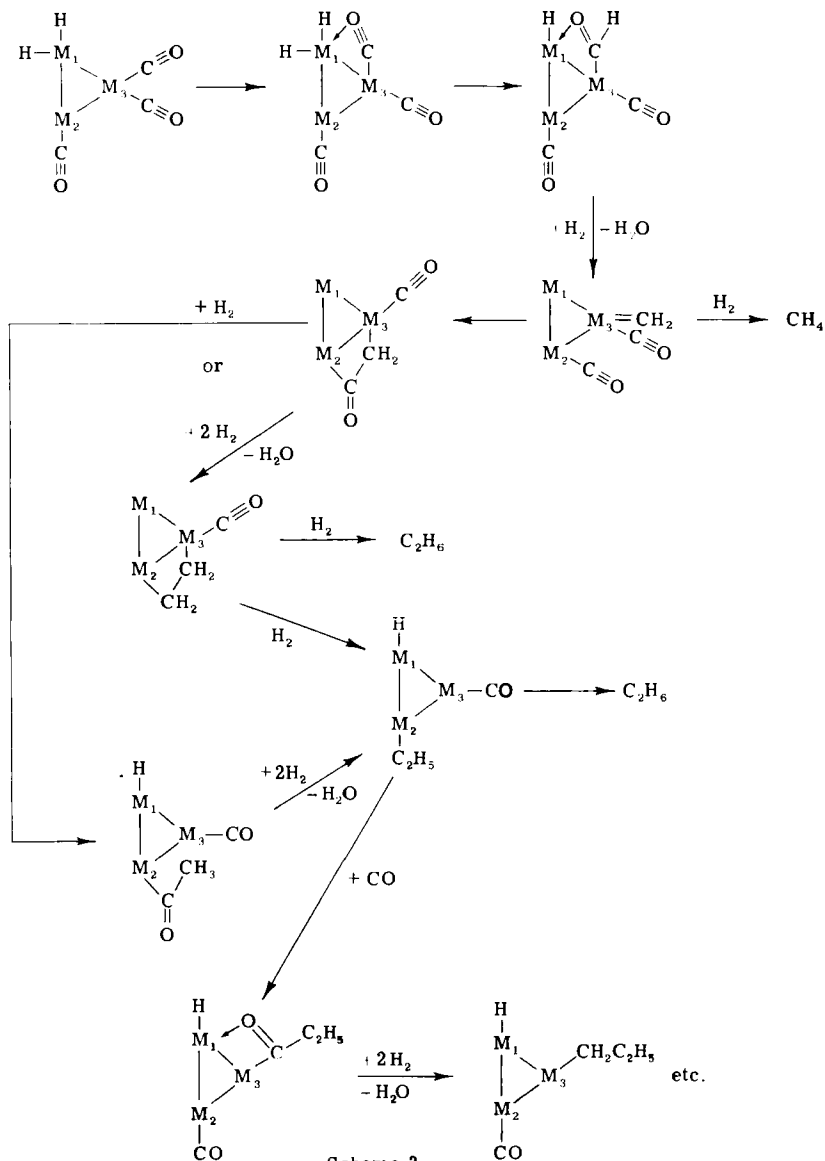
As discussed in Section II,C,1 using the simple mechanistic picture



the ratio k_1/k_2 , related to the hydrocarbon product distribution, can be determined. Good experimental agreement is obtained (see Fig. 2) for the higher hydrocarbon products, although it is generally found that the quantity of methane produced is considerably greater than that expected on the basis of the value of k_1/k_2 ratio. This suggests the existence of an alternative route leading to methane. If we assume that the first propagation step, i.e., formation of a C_2 product, involves carbene attack on carbonyl carbon (intermediate **36**, and if we consider that carbene hydrogenation to methane is a competing reaction, then the origin of high methane production can be explained on the basis of the sequence shown below:



If $k_2' \gg k_1'$, then the amount of methane produced will always exceed that expected on the basis of the k_1/k_2 level. Thus, in agreement with experiment, only C_3 products and above will follow the k_1/k_2 prediction; and in the experimentally found k_1/k_2 ratio, k_1 refers to propagation from C_2 onward and only after C_2 is the single-termination rate constant, k_2 , applicable.



A possible mechanistic pathway for the $M_3(CO)_{12}$ ($M = Ru$ or Os) Fischer–Tropsch catalysts is presented in Scheme 3. It should be emphasized that most of the ideas outlined above are extremely speculative. However, it is to be hoped that with the advent of homogeneous catalyst systems, detailed kinetic and mechanistic studies will lead to a clarification of the situation in the not-too-distant future.

IV

NEW TECHNOLOGY

A. Methanol to Gasoline

A recent development, which could lead to a reassessment of the Fischer–Tropsch reaction as a route to gasoline range product, is the announcement by Mobil of a direct route from methanol to hydrocarbons and water (101):



The hydrocarbons produced are aliphatic and aromatic and are predominantly in the gasoline boiling range (C_4 – C_{10}).

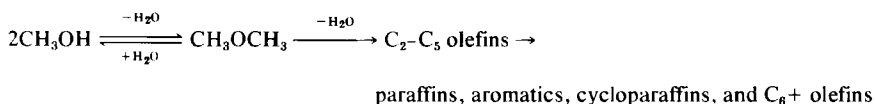
The production of methanol from synthesis gas is a well-established process (23, 102), and there have been predictions that methanol itself could become the fuel of the future (103). Whether or not this prediction will prove correct is debatable⁴; meanwhile, Mobil suggests that coupling known methanol production technology with their new process provides an economically attractive alternative to both Fischer–Tropsch fuels and direct utilization of methanol (104).

The catalyst used for the conversion of methanol to gasoline is based on a new class of shape-selective zeolites (105–108), known as ZSM-5 zeolites, with structures distinctly different from other well-known zeolites. Apparently, the pore dimensions of the ZSM-5 zeolites are intermediate between those of wide-pore faujasites (ca. 10 Å) and very narrow-pore zeolites such as Zeolite A and erionite (ca. 5 Å) (109). The available structural data indicate a lattice of interconnecting pores all having approximately the same diameter (101). Hydrocarbon formation

⁴ Methanol suffers from a number of disadvantages compared to gasoline. It is toxic and corrosive and has a high affinity for water. The energy content of 1 gallon of methanol is only approximately half that of 1 gallon of gasoline. Furthermore, a switch from gasoline to methanol as an automotive fuel would involve considerable downstream investment in terms of engine modification together with storage and distribution facilities.

over ZSM-5 is not limited to the use of methanol as feed. A wide range of organic compounds—e.g., *tert*-butanol, 1-heptanol, propanaldehyde, and acetone—can also be converted to hydrocarbon products, although from an economic standpoint methanol is probably the most attractive feedstock. Under typical process conditions, crude methanol containing ca. 17 wt% water is converted into a gasoline fraction containing highly branched paraffins (51%), highly branched olefins (13%), naphthenes (8%), and aromatics (28%) (104). In addition to the gasoline fraction (ca. 75%), low-boiling hydrocarbons (C_1 – C_4) together with small amounts of CO, CO_2 , and coke are also formed. The hydrocarbons produced have a relatively narrow range of molecular weights, terminating abruptly at about C_{10} . It is suggested that this limited distribution results from the unique molecular shape selectivity of the ZSM-5 zeolites (101). The overall stoichiometry of the process corresponds to that expected on the basis of Eq. (26).

In a recent publication, Chang and Silvestri have discussed this reaction in detail (109). They reported that under conditions of low (ca. 10%) conversion substantial amounts of dimethyl ether, formed by the reversible dehydration of methanol, are present and 78% of the primary hydrocarbon product consists of C_2 – C_4 olefins. Also, if dimethyl ether, in the absence of water, is used instead of methanol, essentially the same hydrocarbon product distribution is obtained. On the basis of these observations, Chang and Silvestri suggest the reaction path shown below:



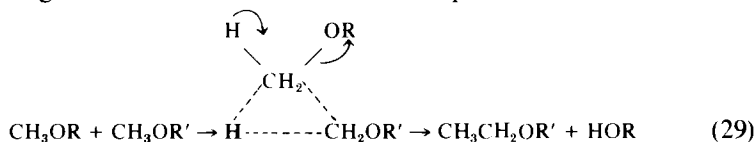
It is proposed that the primary step in the formation of olefins involves the formation of a carbenoid species, $[:CH_2]$, which then inserts into a C—H bond of either methanol or dimethyl ether:



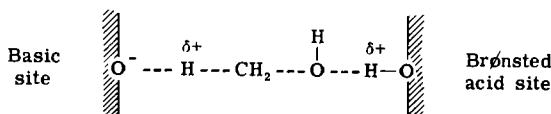
where $R = H$ or CH_3 . Acid-catalyzed elimination of ROH yields the product olefin:



In the ZSM-5 case, production of the carbene and insertion into the C—H bond is thought to be a concerted bimolecular process:



where R, R' = H or alkyl, with the methylene donor being labilized by the zeolite crystal field. As pointed out by Chang and Silvestri, α -elimination reactions have previously been proposed to explain the production of olefins from methanol over H-mordenite (110). Swabb and Gates have suggested a concerted process (111), involving both Brønsted acidic and basic sites in the zeolite, i.e.,



Although the mechanism proposed for the ZSM-5/methanol system adequately explains the production of the primary C_2 – C_5 products, it is not clear how these are converted into the final gasoline product or indeed why this product should be so rich in aromatics. Production of olefins from methanol over zeolite catalysts has previously been described (110, 112); however, the ZSM-5 system appears to be unique with respect to both product selectivity and catalyst stability. Mobil now has some 140 patents relating to the preparation and use of ZSM-5 zeolites and has stated that “given a favorable economic and political climate” a commercial unit could be in operation by the early 1980’s (101).

B. Production of Lower, C_2 – C_4 , Olefins from Synthesis Gas

Although it is generally accepted that the production of fuels via the classical Fischer–Tropsch synthesis is not likely to be economically attractive in western Europe within the next decade, it has been suggested that the selective production of C_2 – C_4 olefins from coal-derived synthesis gas is an economic proposition, even at the present-day price of German brown coal (113). If we accept that carbenoid species are intermediary in the Fischer–Tropsch reaction, then catalysts leading to the selective production of at least ethylene should be feasible. The $Ir_4(CO)_{12}/NaCl \cdot 2AlCl_3$ systems discussed earlier in this chapter could be viewed as a promising lead in this area. With respect to heterogeneous catalysts, selectivities to C_2 – C_4 products of the order of 85% have been claimed (114, 115). Ruhrchemie has disclosed that a mixture, consisting of an iron oxide (e.g., Fe_2O_3 , Fe_3O_4), a titanium oxide (e.g., TiO_2), zinc oxide, and potassium carbonate in the approximate ratio 100 Fe:25 Ti:10 ZnO:4 K_2O , after heating at 1050°C and then reducing with hydrogen at 500°C, catalyzes the conversion of a 1:1 mixture of carbon monoxide and hydrogen at 340°C/10 bar to a mixture consisting of ethane (33.4 wt%),

propene (21.3 wt%), butene (19.9 wt%) together with 10.1 wt% methane and 9.9 wt% saturated C_2 - C_4 hydrocarbons (114). These results were obtained at a CO/H_2 conversion of 87%. The important factor responsible for modifying the behavior of the iron catalyst is thought to be the presence of the TiO_2 . Similarly, Kölbel and Tillmetz have recently shown that manganese-based catalysts are active for the production of C_2 - C_6 alkenes from CO/H_2 mixtures (115). This latter finding is especially surprising because, although the use of manganese as a catalyst promoter has been widely recognized (4), it has not previously been reported as a Fischer-Tropsch catalytically active element. Kölbel and Tillmetz claim that metallic manganese, prepared electrolytically (99.2% pure), after being heated at $380^\circ C$ in the presence of CO (49.2%), H_2 (46.3%), and He (4.5%) at 1 atmosphere for 24 hours, catalyzes the conversion for CO/H_2 at $320^\circ C/10.2$ bar to a mixture of C_1 - C_5 hydrocarbons consisting of 57% olefinic products. Interestingly, the major olefinic product is butene (yield 13.4 g/Nm^3), followed by ethene (6.7 g/Nm^3) and propene (4.0 g/Nm^3). Increasing the temperature to $375^\circ C$ results in both an increase in selectivity (57% to 65%) to olefinic products and a change in the ethene, propene, butene ratio (yields at $375^\circ C$; ethene, 23.8 g/Nm^3 ; propene, 8.2 g/Nm^3 ; butene, 17.7 g/Nm^3). By modifying the operating conditions and catalyst constitution, selectivities of the order of 90% to C_2 - C_4 olefin products have been obtained. Thus, with a manganese/iron precipitation catalyst having an $Mn:Fe$ ratio of 9:1 at $330^\circ C/1.5$ bar and a CO/H_2 conversion of 33%, the yield of hydrocarbon products (in g/Nm^3) was: ethene, 10.7; ethane, 1.3; propene, 16.1; propane, 2.1; and butene 2.7. Only traces of methane and liquid products were obtained. In all the examples given in their patent application, methane production is low compared to the C_2/C_3 production; in several cases, propene is the major gaseous product (115). This represents a marked deviation from what is normally observed with heterogeneous Fischer-Tropsch catalyst systems and may be indicative of a mechanism involving carbenoid-type intermediates similar to that proposed (*vide supra*) for the homogeneous systems.

V

SUMMARY

In the 16th Century an energy crisis sparked off by an 800% increase in the price of wood saw the beginning of the use of coal as a source of energy (2). A 20th-Century energy crisis involving a "modest" 300% increase in the price of oil has rekindled interest in coal, has focused

attention on the use of synthesis gas as feedstock for the oil and chemical industries, and has brought the Fischer-Tropsch reaction back into the limelight. In this article an attempt has been made to highlight some of the recent advances in this field. Special attention has been given to homogeneous systems which are either capable of catalyzing the reactions between carbon monoxide and hydrogen or which provide some insight into how these two molecules can be induced to interact at metal center(s). All the homogeneous catalyst systems discussed are at a preliminary stage of development; yet it is perhaps significant that in all cases more than one metal center is thought to be involved in the catalytic species. Whether the presence of more than one metal will prove a prerequisite for homogeneous Fischer-Tropsch catalysts must await experimental verification. However, as a working hypothesis it suggests many exciting possibilities. Carbon monoxide and hydrogen are two of the most widely studied molecules in homogeneous catalysis, cf. hydroformylation, carbonylation, hydrogenation. The design of systems capable of persuading them to interact in a selective manner remains a worthwhile challenge for the organometallic chemist.

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Selectivity Control in Nickel-Catalyzed Olefin Oligomerization

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I

INTRODUCTION

Catalytic reactions, both homogeneous and heterogeneous, are usually characterized by a diversity of reaction paths and consequently of reaction products. One of the problems encountered in catalytic reactions is that of selectivity control, i.e., how to achieve a high selectivity with respect to a desired reaction product.

Homogeneously catalyzed reactions can in general be more easily controlled than the corresponding heterogeneous reactions because the reaction temperature is usually lower and the catalyst system better defined. These are requirements which have attracted attention in recent years in connection with energy considerations (1).

In the case of homogeneous catalyst systems, it is frequently possible to vary the catalyst composition and thereby some structural features of the catalyst in a systematic manner. The study of the influence of such modifications on the nature and the distribution of the products is an important method for improving the efficiency of a homogeneous catalyst and is often referred to as the "tailoring of a catalyst" (2). Such inves-

tigations frequently give important mechanistic information on the relationship between the catalyst structure and its activity.

Dimerization, oligomerization, and similar reactions of olefins have been reported to be catalyzed by systems involving the majority of the Group VIII metals (3). The reasons for the particular interest in nickel-containing catalysts are their exceptionally high catalytic activity (catalytic reactions have been performed at temperatures as low as -100°C), the diversity of catalytic reactions of obvious synthetic value, as well as the possibility to direct the course and control the selectivity of a catalytic reaction by "tailoring the catalyst" which are perhaps without parallel among transition metal complex catalysts.

In the present chapter an attempt is made to summarize the available material concerning the control of selectivity in the nickel-catalyzed homogeneous oligomerization of olefins and related reactions [for a previous review of this topic, see Bogdanović *et al.* (4)]. No attempt has, however, been made to give a complete literature survey.

The Nature of Selectivity Control

In this section we are concerned with the problems usually encountered in olefin oligomerization and related reactions. The product of the catalytic dimerization of a single olefin, such as ethylene, is in general a mixture of dimers with lesser amounts of higher oligomers. It is frequently possible to control the *selectivity of dimerization vs. oligomerization*—that is, the percentage of dimers in the product. It is appropriate here to note that it is still not possible catalytically to convert olefins, such as ethylene, selectively to open-chain oligomers other than dimers, even though highly selective *cyclooligomerization* reactions, such as the cyclotetramerization of acetylene and cyclotrimerization of butadiene (5), are known.

The product of the dimerization of an unsymmetrical substituted olefin, such as propene, is dependent on the direction of coupling of the two olefinic units; in general, a mixture of isomers is obtained. In order to obtain a high yield of a particular dimer, the control of the regioselectivity of the individual addition steps in the catalytic cycle or even the reversal of the direction of addition in consecutive steps is required (Section IV,E).

The number of possible products formed on dimerization is increased as the result of double-bond isomerization which may occur before, after, or during the reaction. In order to obtain a particular dimer in high

selectivity, it is necessary to control the relative rates of dimerization vs. double-bond isomerization.

The selectivity problem is particularly important in the dimerization of two different olefins when, in addition to the required codimers, a mixture of the two possible homodimers may be produced.

A particularly challenging situation in catalysis in general and in olefin oligomerization in particular is that of stereoselectivity control, including diastereoselectivity and enantioselectivity (6).

It is apparent from this short introduction that optimal control of the overall selectivity of olefin oligomerization reactions depends on the simultaneous control of several different types of selectivity.

II

METHODS OF PREPARATION AND SOME FEATURES OF NICKEL CATALYSTS ACTIVE FOR THE OLIGOMERIZATION OF OLEFINS AND RELATED REACTIONS¹

The homogeneous nickel catalysts discussed here² have been prepared from a variety of nickel compounds; the methods of preparation can be classified as follows:

(A) Ziegler method: Catalyst systems can be prepared by reacting a nickel(II) salt with an organometallic compound of the main group metals but aluminum is preferred.

(B₁): Treatment of an organo- or a hydrido-nickel(II) compound with a Lewis acid. Organometallic compounds, such as alkylaluminum halides, which have Lewis acid properties, can also be used.

(B₂): Metathetical exchange of a nickel(II)-bonded anionic ligand by an anion of a stronger Brønsted acid. The nickel(II) component can be either an organonickel complex or a nickel hydride.

(C₁): Treatment of zero-valent nickel complexes with Brønsted acids.

(C₂): Treatment of zero-valent nickel complexes with Lewis acids, whereby the Lewis acid can also be an organometallic species.

(D): Reaction of nickel(I) compounds with Lewis acids.

These homogeneous catalysts can in addition contain a Lewis base, such as a phosphine or phosphite, and can accordingly be divided into

¹ Included are the dimerization, codimerization, oligomerization, double-bond isomerization, and cyclization of olefins.

² These catalysts should be clearly distinguished from those active for the cyclooligomerization of conjugated dienes, etc., which are based on zero-valent nickel compounds (5, 7, 8).

electron-donor-free and *electron-donor-modified* catalysts. It should, however, be noted that anionic ligands which are present in the starting nickel compound may also possess electron-donor properties and hence can play a dual role, whereby electron-donor properties of such anionic ligands modify the catalyst in the same manner as donor molecules. This is of particular importance for nickel(II) compounds containing chelating anionic ligands such as acetyl acetonate. In addition, the substrate (olefin molecules) can also function as electron donors. Associated with this is the fact that catalyst systems in which electron donors are absent are preferably prepared in the presence of substrate olefins.

It is generally assumed that the electron donor can have one or several of the following functions: to increase the stability of the catalytically active species; to increase the catalytic activity of the catalyst; to allow a control over the selectivity of the catalytic reaction; or to increase the solubility of the catalyst in organic media. The main effect of Lewis or Brønsted acids is to increase the catalyst activity, but their influence on selectivity control is not considered to be of great significance (see, however, Sections IV,D,2 and IV,F). The increase in activity of the catalyst (see below) on the addition of Lewis or Brønsted acids is frequently accompanied by a decrease in stability of the system.

In the following examples a variety of catalysts prepared according to methods (A)–(D) will be discussed.

Method A: Most of the procedures described in the patent literature are based on the Ziegler method. Catalysts of this type, which are particularly active for the dimerization of propene and the oligomerization of ethylene, are obtained by reacting nickel(II) compounds of the type NiX_2 or L_nNiX_2 (X = anionic ligand, L = donor ligand, $n = 1, 2$ etc.) with an excess of halogen-containing organoaluminum compounds, such as dialkylaluminum halides, alkylaluminum dihalides, or alkylaluminum sesquihalides³ [e.g., $(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Cl}_3$]. In the presence of nickel(II) halides, it is possible to substitute halogen-containing organoaluminum compounds by triethylaluminum (9).

Ligand-free catalysts have been prepared from the following types of nickel(II) compounds: nickel salts of long-chain aliphatic or aromatic carboxylic acids (10, 11) or of sulfonic acids (11), nickel enolates of β -diketones (11) [e.g., nickel acetylacetonate (4, 12)] or their imino derivatives (11, 13), nickel phenolates (11), dithiocarbamates (14), and mercaptides (15).

Phosphine-modified catalysts have been prepared from phosphine ad-

³ Dialkylaluminum halides, alkylaluminum dihalides, and alkylaluminum sesquihalides will be referred to henceforth as "alkylaluminum halides."

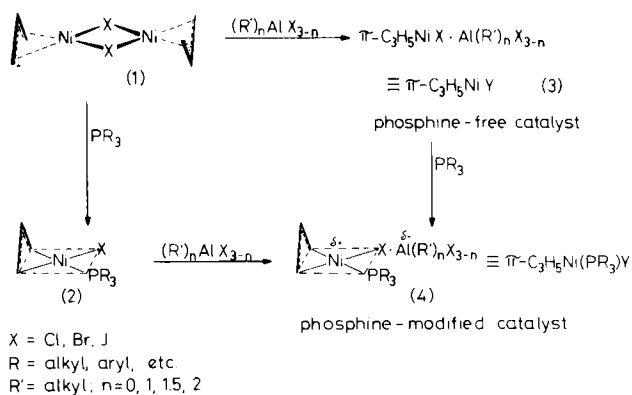
ducts of nickel halides $(R_3P)_2NiX_2$ (16–22) [with water (23, 24) or organic halides (25) as promoters] and ionic complexes of the type $R_3R'P^+[(R_3P)NiCl_3]^-$ ($R, R' =$ organic groups) (26–28). Alternatively, the above-mentioned nickel(II) compounds may be reacted with alkylaluminum halides in presence of phosphines or phosphites (12, 13, 17, 29–39).

Not only phosphines or phosphites but also phosphoric acid trisdialkylamides (40), sulfoxides (41), etc. have been used as electron donors in the preparation of the catalyst. In addition, the catalytic activity of tetramethylcyclobutadienenickel dichloride and alkylaluminum halides has been studied in detail (42, 43).

Nickel-based Ziegler catalysts can be prepared using halogen-free organoaluminum compounds of low Lewis acidity, e.g., dialkylaluminum alkoxides. However, the catalytic properties of these systems differ remarkably from those described above. The nickel components in such a case may be nickel acetylacetonate, or the nickel enolates of various other β -dicarbonyl compounds (44, 45), in particular such halogenated β -dicarbonyl compounds as hexafluoroacetylacetone (44, 46).

Method B₁: Highly active homogeneous catalysts may be prepared by activating either organonickel compounds of the type $RNi(L)_nX$, $R_2Ni(L)_n$ or nickel hydrides $H-Ni(L)_nX$ ($R =$ organyl group, $X =$ anionic ligand, $L =$ donor ligand, $n = 0, 1, 2, 3$ etc.) with strong Lewis acids.

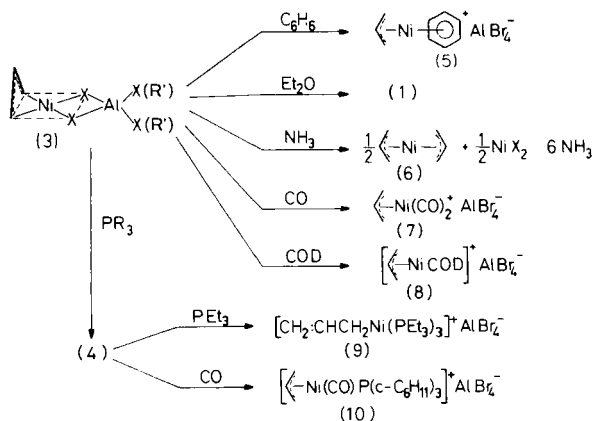
The primary (7, 47) and most commonly used organonickel compounds have been the dimeric π -allyl- (or substituted π -allyl-) nickel halides (1) (Scheme 1) or their monophosphine adducts (2) in the presence of Lewis acids such as aluminum halides or alkylaluminum halides (4, 48–53). The



SCHEME 1

reaction between π -allylnickel halides (1) or their phosphine adducts (2) with aluminum halides or alkylaluminum halides in a solvent such as chlorobenzene leads to complexes 3 and 4. The phosphine-modified catalysts (4) can also be prepared by adding one equivalent of phosphine to the phosphine-free catalyst (3). The negatively charged component of complexes 3 and 4, i.e., the aluminum atom with its surrounding ligands, or of analogous complexes (see Section IV,D,2), will be referred to as the "complex anion" of the catalyst and will be designated by "Y." In the case where the Lewis acid is an alkylaluminum dihalide, it is probable that the "complex anion" involves more than one aluminum atom (51).

The structure of the complex (3) formed between the π -allylnickel halides and an aluminum halide or an alkylaluminum halide is not known with certainty; a reasonable suggestion is shown in Scheme 2. This proposal is based on the known structure of the dimeric π -allylnickel halides (54) and on that of the related phosphine-containing complex (4a) (Fig. 1). The presence of a π -allyl system in 3 (X = Br) has been confirmed by ^1H NMR spectroscopy. The weakly polar character of 3 accounts for the poor solubility in hydrocarbons and good solubility in polar, nonbasic solvents such as chlorobenzene or dichloromethane. If prepared in aromatic hydrocarbons such as benzene or toluene, then 3 separates out as red, solvent-containing oil (52). From the reaction of π -allylnickel bromide with aluminum bromide in benzene, a red compound suggested to have the ionic structure 5 has been obtained (55). The complexes 3 are decomposed by ethers, amines, or ammonia (Scheme 2), while from the reaction with ethers π -allylnickel halides (1) can be regenerated. Cleavage followed by disproportionation of the resulting π -



SCHEME 2

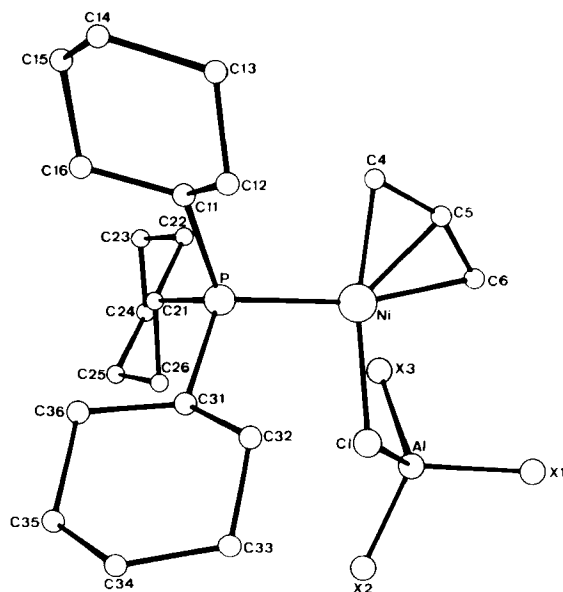


FIG. 1. Molecular structure of the complex (**4a**) comprising π -allylnickel chloride, tricyclohexylphosphine, and methylaluminum dichloride.

allylnickel halide to bis(π -allyl)nickel (**6**) is observed on reacting **3** with ammonia. Bis(π -allyl)nickel is volatile and can be distilled off (53, 56), and this reaction (Section III) has been applied as a diagnostic tool to detect the presence of a nickel-bonded π -allyl group in the reaction mixture.

It is generally assumed that the Lewis acid in **3** decreases the charge on the metal, i.e., increases its electrophilicity. The removal of charge from the nickel allows additional electron donors to coordinate to the nickel atom, and reaction with, for example, 2 moles of carbon monoxide or 1 mole of 1,5-cyclooctadiene (COD) gives the insoluble, catalytically inactive and presumably ionic complexes **7** and **8**. In contrast, π -allylnickel halides (**1**) add only 1 mole of carbon monoxide while they do not react with COD (52).

Reaction of **3** with 1 equivalent of a phosphine results in formation of "phosphine-modified" catalysts (**4**). The complex formed from π -allylnickel chloride, tricyclohexylphosphine, and methylaluminum dichloride (**4a**) has been isolated and its structure determined crystallographically (see Fig. 1) (57): The phosphine is bonded to the nickel atom, and interaction with the Lewis acid takes place via a chlorine bridge. The bridging chlorine atom is almost symmetrically bound to both the nickel

and the aluminum atoms. The ligands adapt essentially a square-planar arrangement around the nickel, two coordination positions being occupied by the allyl group and the remaining ones by the phosphine and the chlorine ligand. The geometry around the aluminum atom is tetrahedral.

The phosphine ligand has a profound influence on both the activity and selectivity of the catalyst system (Section IV), and by a suitable choice different types of selectivities (e.g., regio- and enantioselectivity) can be influenced, indicating strongly that the phosphine molecule remains complexed during the catalytic reaction. Addition of further phosphine or carbon monoxide to **4** leads (unless an excess of alkylaluminum halides is present) to catalytically inactive systems such as **9** and **10** (Scheme 2) (52), suggesting that the catalytically active species has only *one* phosphine ligand complexed to the nickel atom. This is supported by the fact that bidentate phosphine ligands, such as $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, deactivate the catalyst (51).

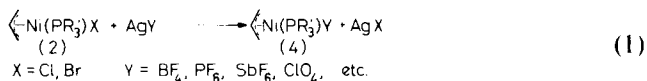
The behavior of **3** toward ether or amines on the one hand and toward phosphines, carbon monoxide, and COD on the other (Scheme 2), can be qualitatively explained on the basis of the HSAB concept⁴ (58). The decomposition of **3** by ethers or amines is then seen as the displacement of the halide anion as a weak "hard base" from its acid-base complex (**3**). On the other hand, CO, PR_3 , and olefins are "soft bases" and do not decompose (**3**); instead, complexation to the nickel atom occurs. The behavior of complexes **3** and **4** toward different kinds of electron donors explains in part why they are highly active as catalysts for the oligomerization of olefins in contrast to the dimeric π -allylnickel halides (**1**) which show low catalytic activity. One of the functions of the Lewis acid is to remove charge from the nickel, thereby increasing the affinity of the nickel atom for "soft donors" such as CO, PR_3 , etc., and for substrate olefin molecules. A second possibility, an increase in reactivity of the nickel-carbon and nickel-hydrogen bonds toward complexed olefins, has as yet found no direct experimental support.

Examples of π -allylnickel-X compounds (X = anionic ligand) other than π -allylnickel halides which have been used in combination with (alkyl)aluminum halides as olefin oligomerization catalysts are π -allylnickel acetylacetonate (**11**) (Section III), π -allylnickel aziridide (**4**, **56**), and bis(π -allyl)nickel (**6**) (59). In addition to π -allylnickel halides, organonickel halides such as tritylnickel chloride (**60**, **61**) and pentafluorophenylbis(triphenylphosphine)nickel bromide (**62**), or hydridonickel halides, e.g., *trans*-hydridobis(triisopropylphosphine)nickel chloride (**12**) (Section III), give active catalysts after activation with aluminum halides

⁴ The HSAB concept is the hard-soft acid-base concept.

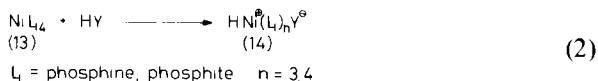
or alkylaluminum halides (63). Other Lewis acids, such as TiCl_4 (64), SbF_5 (65), BF_3 , or $\text{BF}_3 \cdot \text{OEt}_2$ (63, 66) have also been used. For the sake of completeness it should be mentioned that some organonickel complexes, such as cyclooctatrienylnickel chloride (7) or π -cyclopentadienyl- π -cyclopentenylnickel (67) show low catalytic activity in the absence of Lewis acids.

Method B₂: A modification of method B₁ for the preparation of catalysts starting from organonickel halides consists in the exchange of the halide anion by an anion of a strong complex acid, HY. This has been accomplished by reacting π -allylnickel halides (1) or their phosphine adducts (2) with silver salts (65):

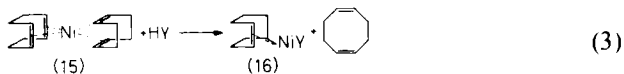


Phosphine-free catalysts of this type are of low thermal stability, and the exchange reaction is performed preferentially in the presence of olefins. *trans*-Pentachlorophenylbis(triphenylphosphine) nickel chloride undergoes a similar reaction (68).

Method C₁: Catalysts for the dimerization and oligomerization of olefins and for the isomerization of olefinic double bonds may be obtained by reacting zero-valent nickel complexes with Brønsted acids. Particular attention has been given to catalysts prepared from tetrakis(aryl)-, trialkylphosphine, or trialkylphosphite nickel(0) complexes (13) and HBF_4 (69, 70). $\text{BF}_3 \cdot \text{Et}_2\text{O} \cdot \text{H}_2\text{SO}_4$, $\text{BF}_3 \cdot \text{C}_2\text{H}_5\text{OH}$, $\text{BF}_3 \cdot \text{H}_2\text{O}$ (69), H_2SO_4 , $\text{CF}_3\text{CO}_2\text{H}$, HCN , $\text{HCN} \cdot \text{ZnCl}_2$, HAlCl_4 (70). In several cases (70–72) it has been shown spectroscopically that oxidative addition of the Brønsted acid to the nickel atom with formation of a cationic hydridonickel(II) complex (14) occurs:



For the preparation of catalysts using zero-valent nickel olefin complexes, bis(1,5-cyclooctadiene)nickel (COD_2Ni) (15) as a nickel(0) source and Brønsted acids (such as $\text{CF}_3\text{SO}_3\text{H}$ and HBF_4) have been used. From the reaction of COD_2Ni with $\text{CF}_3\text{SO}_3\text{H}$, the nickel complex 16 ($\text{Y} = \text{CF}_3\text{SO}_3$) can be isolated (65).



Method C₂: Nickel catalysts for olefin oligomerization may also be

prepared by treating phosphine or phosphite zero-valent nickel complexes or $\text{Ni}(\text{CO})_4$ with an excess of Lewis acids such as aluminum halides, alkylaluminum halides, or BF_3 (69, 73–78). The activity of these catalysts is relatively low but may be increased by the addition of a Brønsted acid (69).

Method D: $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{NiCl}$ in conjunction with AlCl_3 or $\text{BF}_3 \cdot \text{OEt}_2$ is catalytically active (69, 73).

III

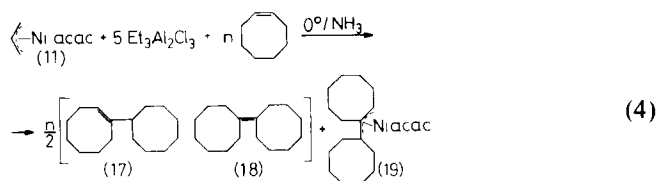
FORMATION AND PROBABLE STRUCTURE OF THE CATALYTICALLY ACTIVE SPECIES

There can be little doubt that the active species involved in most or even all of the various combinations described in Section II is $\text{HNi}(\text{L})\text{Y}$ (see below), because the different catalysts prepared by activating the nickel with Lewis acids have been shown to produce, under comparable conditions, dimers and codimers which have not only identical structures but identical compositions. On modification of these catalysts by phosphines, the composition of dimers and codimers changes in a characteristic manner independent of both the method of preparation and the nickel compound (2, 4, 7, 16, 17, 26, 29, 42, 47, 76). Similar catalysts are formed when organometallic or zero-valent nickel complexes are activated with strong Lewis acids other than aluminum halides or alkylaluminum halides, e.g., BF_3 .

Evidence has been collected over the years which strongly indicates that the active species in the oligomerization reactions are nickel–hydride and nickel–alkyl complexes. [This is not necessarily true for catalysts prepared from nickel(II) compounds and organoaluminum compounds having low Lewis acidity, e.g., $(\text{C}_2\text{H}_5)_2\text{AlOC}_2\text{H}_5$ (44).] The majority of the evidence is circumstantial and is discussed below.

An obvious method to investigate the formation and the nature of the catalytically active nickel species is to study the nature of products formed in the reaction of complexes such as **3** or **4** with substrate olefins. This has been investigated in some detail in the case of the catalytic dimerization of cyclooctene to 1-cyclooctylcyclooctene (**17**) and dicyclooctylidene (**18**) [Eq. (4)] using as catalyst π -allylnickel acetylacetonate (**11**) or π -allylnickel bromide (**1**) activated by ethylaluminum sesquihalide or aluminum bromide (**4**). In a typical experiment, **11** in chlorobenzene was activated with excess ethylaluminum sesquichloride; cyclooctene was then added at 0°C and the catalytic reaction followed by removing

aliquots from the solution, destroying the catalyst with ammonia, and determining the extent of cyclooctene conversion. At the same time, the nature and concentration of soluble nickel compounds left in the solution after destruction of the catalyst with ammonia were determined. Treatment of a sample of the catalyst solution with ammonia before addition of cyclooctene resulted in formation of bis(π -allyl)nickel (80–90%) (see Scheme 2), indicating that at this stage the catalyst mixture still contains the original π -allylnickel compound (**11**). When, however, the catalyst is treated with ammonia shortly after cyclooctene addition, metallic nickel precipitates and only traces of nickel can be detected in the solution. After conversion of 30–50 moles cyclooctene/mole nickel catalyst, the catalyst is practically inactive. This decrease of catalytic activity is accompanied by an increase in the concentration of a new π -allylnickel complex (**19**) [Eq. (4)], derived from the cyclooctene dimer. After termination of the catalytic reaction the concentration of **19** in the solution remains constant, and this complex can be isolated in 70–80% yield by treating the solution with aqueous ammonia.



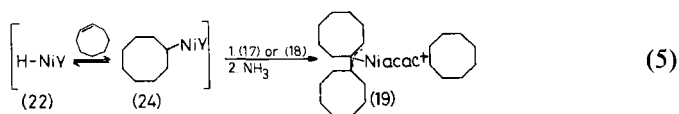
Treatment of **19** with ethylaluminum sesquichloride or aluminum bromide results in the formation of a new catalyst, which is active for the dimerization of olefins such as ethylene or propene but inactive for the dimerization of cyclooctene.

The following conclusions can be drawn: (a) π -Allylnickel compounds are probably not involved in the catalytic dimerization of cyclooctene, because the highest reaction rate occurs when only traces of these compounds can be detected; further, the concentration of the new π -allylnickel compound (**19**) becomes significant only after the catalytic reaction has ceased. (b) The complex formed between the original π -allylnickel compound (**11**) and the Lewis acid is transformed immediately upon addition of cyclooctene to the catalytically active nickel complex or complexes. In contrast to π -allylnickel compounds, this species decomposes to give metallic nickel on treatment of the catalyst solution with ammonia. (c) The transformation of the catalytically active nickel complex to the more stable π -allylnickel complex occurs parallel with the catalytic dimerization reaction. This process is obviously of importance in stabilizing the catalyst system in the absence of reactive olefins. In

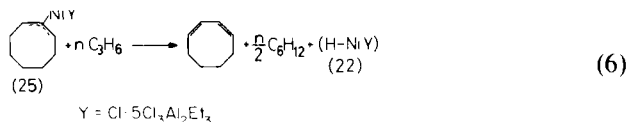
the case of the dimerization of cyclooctene, the formation of the π -allylnickel derivative (19) limits the turnover number of the catalyst.

In order to investigate the fate of the allyl group in 11 during its transformation to the active catalyst, experiments similar to those described above were performed at -40°C , at which temperature the rate of cyclooctene dimerization is extremely low. Compound 11 or 1 ($\text{X} = \text{Br}$) was activated with ethylaluminum sesquichloride or aluminum bromide, and at -40°C cyclooctene followed by aqueous ammonia was added: Metallic nickel precipitated almost quantitatively, indicating that here also the original π -allylnickel compound (11 or 1) has been almost completely transformed to the catalytically active species. At this temperature, however, only traces of cyclooctene had been dimerized, and 80–85% of the allyl group originally bonded to nickel in 11 or 1 can be recovered in the form of the bicyclo[6.3.0]octenes 20 and 21 (Scheme 3). This result suggests that the allyl group originally bonded to nickel reacts in an initial reaction with cyclooctene to give the catalytically active species. No hydrogen evolution is observed during the addition of cyclooctene; therefore, these experiments can be taken as strong evidence for the intermediate formation of a hydridonickel species (22) whose formation from 23 can be formulated as shown in Scheme 3. The reaction sequence (Scheme 3) is supported by the formation of 20 and 21 either from 3-allylcyclooctene (Section IV,D) or as a by-product of the codimerization of 1,3-cyclooctadiene with propene (4, 79). The hydridonickel species (22) is probably stabilized by complexation with cyclooctene molecules and is likely to be in equilibrium with an alkyl form (24); it decomposes on treatment with ammonia to give metallic nickel.

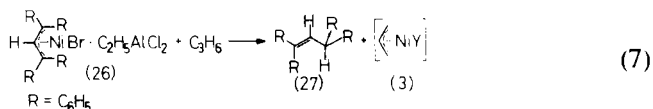
The transformation of the catalytically active species (21 or 24) into the complex (19) at the end of the catalytic reaction requires the abstraction of a hydrogen atom from the cyclooctene dimer and is accompanied by hydrogenation of the monomer to give cyclooctane [Eq. (5)]:



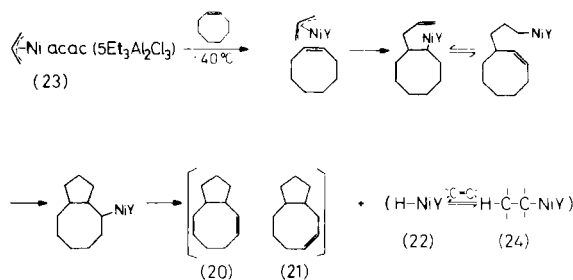
That the sequence shown in Scheme 3 is not the only pathway available for $\text{H}-\text{NiY}$ formation is indicated by the isolation of 1,3-cyclooctadiene from the reaction products of the dimerization of propene with the π -cyclooctenylnickel system (25) (80): it seems reasonable that the $\text{H}-\text{NiY}$ species 22 in this case is at least in part formed through direct elimination from 25 without prior monomer insertion into the $\text{Ni}-\text{C}$ —bond [Eq. (6)]:



Yet another possibility is illustrated by the propene (or ethylene) dimerization catalyzed by π -1,1,3,3-tetraphenylallylnickel bromide (**26**) activated with ethylaluminum dichloride; the isolation of considerable amounts of 1,1,3,3-tetraphenylpropene (**27**) from the reaction mixture suggests that a hydrogen atom has been transferred from the substrate olefin to the sterically hindered 1,1,3,3-tetraphenylallyl system under formation of **3** [Eq. (7)] (81). The subsequent formation of the HNiY species from **3** can then take place by insertion of a second propene molecule and β -hydrogen elimination, as discussed above.

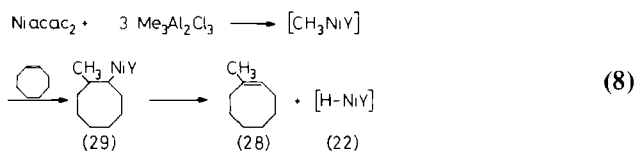


Information concerning the nature of the active species present in catalysts prepared according to method A has also been obtained from a study of cyclooctene dimerization in the presence of nickelacetylacetonate ($\text{Ni}(\text{acac})_2$) and methyl- or ethylaluminum sesquichloride. When $\text{Ni}(\text{acac})_2$ instead of π -allylnickelacetylacetonate (**11**) is the catalyst component, no difference in the course of cyclooctene dimerization, either in the turnover number or in the formation of **19**, is observed (4). The pathway for formation of the NiHY species is, however, different: using methylaluminum sesquichloride in combination with $\text{Ni}(\text{acac})_2$ as dimerization catalyst, 1-methylcyclooctene (**28**) is formed in 56% yield (based



SCHEME 3

on Ni(acac)₂). This can be interpreted as being the result of β -hydrogen elimination from nickel alkyl species **29** [Eq. (8)]:

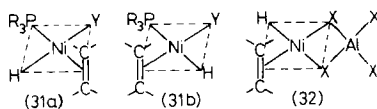


On the other hand, no ethylcyclooctene is formed in the dimerization of cyclooctene using Ni(acac)₂ in combination with ethylaluminum sesquichloride; in this case, the ethylnickel compound first formed undergoes a rapid β -hydrogen elimination reaction, prior to the insertion of cyclooctene into the Ni—C—bond (79). In preparation of catalysts according to method A, the organoaluminum species acts as both alkylating agent and Lewis acid [Eq. (8)]. In contrast, in method B the organoaluminum species acts only as Lewis acid.

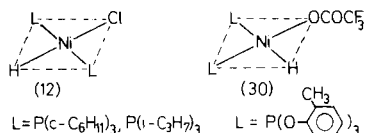
The formation of cationic nickel hydride complexes by the oxidative addition of Brønsted acids (HY) to zero-valent nickel phosphine or phosphite complexes (method C₁) has already been discussed in Section II. Interesting in this connection is a recent ¹H NMR study of the reaction of bis[tri(*o*-tolyl)phosphite]nicklethylene and trifluoroacetic acid which leads to the formation of a square-planar bis[tri(*o*-tolyl)phosphite]hydridonickel trifluoroacetate (**30**) (see below) having a *cis* arrangement of the phosphite ligands (82).

Less clear is the sequence which leads to the formation of the active species in the case of catalysts prepared from zero-valent nickel complexes and aluminum halides or alkylaluminum halides (method C₂). The catalytic properties of these systems, however—in particular, the influence of phosphines (76)—leaves no doubt that the active species is also of the HNiY type discussed above. In this connection, a recent electron spin resonance report that nickel(I) species are formed in the reaction of COD₂Ni with AlBr₃ (83), and the disproportionation of Ni(I) to Ni(II) and Ni(0) in the presence of Lewis acids (69) should be mentioned.

On the basis of the results discussed above and in the Section II, in particular the crystallographic determination of the geometry of complex (**4a**), one is led to suggest that the most probable structure for both the phosphine-modified and the phosphine-free catalyst are **31a**, **31b**, and **32**.



Complex **4a** (see Fig. 1) differs from these catalytically active complexes only in the substitution of the complexed olefin molecules and hydrogen atom by a π -allyl group. The ligands in these square-planar molecules can adopt two different arrangements around the central nickel atom: The olefin can either be trans (**31a**) or cis (**31b**) to the phosphine molecule. Because precedent exists for both these arrangements [e.g., **12** (84) and **30** (82)], it is difficult to decide which of the two structures (**31a** or **31b**) represents the catalytically active species. It is of course possible that the differences observed in the catalytic properties of systems having different ligands L and Y (Section IV) is due (at least in part) to differences in the population of **31a** and **31b**.



From the preceding discussion it is apparent that the control of the selectivity of a catalytic process is possible by varying either the ligand L, the group Y, or both. Of these possibilities, variation of L has been the most extensively studied. The results of these investigations will be discussed in Section IV.

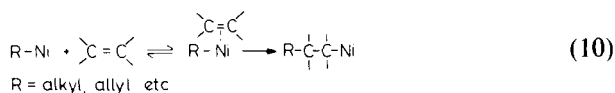
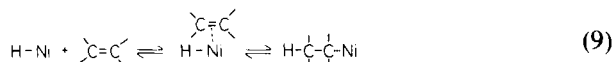
IV

EXAMPLES OF SELECTIVITY CONTROL

A. General Course of Olefin Oligomerization and Related Reactions

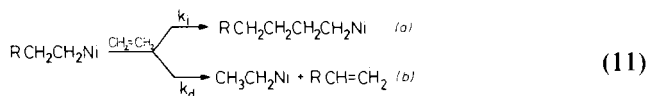
Reactions leading to the formation of the catalytically active nickel hydride species from organonickel precursors (Section III) can be regarded as model reactions for olefin oligomerization reactions. The reactions described by Eq. (8) and Scheme 3 (Section III) show that RNiX compounds (R = methyl or allyl, X = halide or acetylacetonate) activated by Lewis acids add to double bonds under mild reaction conditions (-40° or 0°C). It follows further from these reactions that under conditions leading to olefin dimerization a rapid nickel hydride β -hydrogen elimination reaction occurs. The fact that products resulting from olefin insertion into the nickel-carbon bond are only observed when β -hydride

elimination is suppressed indicates that β -H elimination in these cases is much more rapid than the insertion of an olefin into the nickel-carbon bond. Formation of alkylnickel complexes from cationic (82) or neutral (85) nickel(II) hydrides and olefins has been demonstrated (see Section IV,E). These results show that the olefin oligomerization and related reactions can be explained on the basis of Ni—H and Ni—C addition to olefins followed by β -H elimination [Eqs. (9) and (10)]—a mechanism which is generally accepted. Although the possibility that some of the reaction products are formed by other routes cannot be completely excluded, no experimental evidence for such routes exists and in fact all the products of olefin oligomerization reactions can be satisfactorily explained. Additional support for the mechanism here considered is given by the results of kinetic (33, 42, 64) and deuteration investigations (86, 87) and by a study of ethylene-propene codimerization (66).



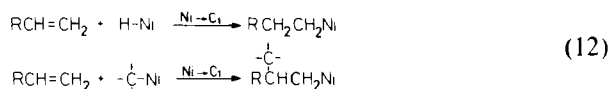
The reversal of the insertion reaction [Eq. (10)] is not normally observed [in contrast to nickel hydride addition to olefins, Eq. (9)]. An exception is the skeletal isomerization of 1,4-dienes (88, 89). A side reaction—the allylhydrogen transfer reaction [Eq. (5)]—which results in the formation of allylnickel species such as **19** as well as alkanes should also be mentioned. This reaction accounts for the formation of small amounts of alkanes and dienes during the olefin oligomerization reactions (51).

The nature and distribution of the products of an olefin oligomerization reaction will depend, *inter alia*, on the relative rate constants of the insertion step (k_i) vs. the displacement step (k_d) [Eq. (11)]:

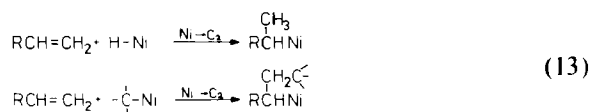


If $k_i \gg k_d$, then, in general, higher oligomers or polymers will be formed; if $k_d \gg k_i$, then olefin dimerization will predominate; if k_i is of the same order of magnitude as k_d , then a mixture of lower oligomers will result. The degree of oligomerization (and the selectivity of dimerization) can thus be controlled by varying the ratio k_i/k_d .

The nature and distribution of the products of the dimerization or oligomerization of unsymmetrical olefins, such as propene, will depend, among others, on the direction of addition of the hydrido- and alkylnickel species to the olefin, i.e., on the regioselectivity of the catalyst (see Section IV,E). In order to define the direction of addition of hydrido- or alkylnickel species to terminal olefins, we shall adopt the convention "nickel-to-C₁ addition" [Eq. (12)] (Ni → C₁):



and "nickel-to-C₂ addition" [Eq. (13)] (Ni → C₂) (51, 90):

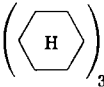


B. The Oligomerization of Ethylene

The reaction of ethylene at -20°C and 1 atm with the phosphine-free catalyst prepared from π -allylnickel chloride and ethylaluminum dichloride in chlorobenzene results in the rapid formation of a mixture of ethylene dimers with lesser amounts of higher oligomers. The dimer fraction consists mainly of 2-butenes and the trimer fraction of 3-methylpentenes and 2-ethyl-1-butene as well as a minor amount of hexene (91). From the composition of the products it can be concluded that the displacement reaction predominates over the insertion reaction when using the phosphine-free catalyst and that the direction of addition of both the H—Ni and C₂H₅—Ni species is mainly of the Ni → C₂ type.

The influence of phosphines on the oligomerization of ethylene using phosphine-modified catalysts prepared from π -allylnickel bromide, ethylaluminum sesquichloride in the presence of phosphine is shown in Table I. The results show that the selectivity of dimerization as well as the degree of oligomerization can be controlled in a wide range by varying the phosphine. The highest selectivity for dimerization (>98%) is achieved using a P(CH₃)₃-modified catalyst. In the sequence of phosphines shown in Table I, a decrease of dimerization selectivity and an increase in the degree of oligomerization are observed; with (*t*-C₄H₉)₂P-i-C₃H₇, 50% of the product consists of tetramers and higher oligomers. As in the case of the phosphine-free-catalyzed reaction, the products of the oligomerization with the phosphine-modified catalyst have mainly a

TABLE I
INFLUENCE OF PHOSPHINES ON THE DIMERIZATION AND
OLIGOMERIZATION OF ETHYLENE^a

PR ₃	C ₄ (%)	C ₈ (%)	C ₈ + higher oligomers (%)
P(CH ₃) ₃	>98	~ 1	—
Pφ ₃	90	10	—
P() ₃	70	25	5
C ₂ H ₅ P(<i>t</i> -C ₄ H ₉) ₂	65	25	10
(<i>i</i> -C ₃ H ₇)P(<i>t</i> -C ₄ H ₉) ₂	25	25	50
P(<i>t</i> -C ₄ H ₉) ₃ ^b	Polyethylene		

^a Catalyst π-C₃H₅NiBr·PR₃-(C₂H₅)₃Al₂Cl₃; -20°C; 1 bar.

^b Ni : P = 1 : 4.

branched-chain structure (4). On the other hand, terminal olefins in the C₄–C₁₈ range having high linearity (>95%) can be prepared by oligomerization of ethylene using catalysts prepared from zero-valent nickel olefin complexes such as COD₂Ni and various phosphines or phosphites having chelating properties, e.g., diphenyl(carbethoxymethyl)phosphine (92) or fluorine-containing ligands (93).

The oligomerization of ethylene with a catalyst modified by P(*t*-C₄H₉)₃ (phosphine:nickel = 1:1) produces the same ethylene oligomers as the phosphine-free catalyst, together with a small amount of polyethylene. The formation of the lower oligomers can be completely suppressed by using a fourfold excess of P(*t*-C₄H₉)₃, with the result that only the above-mentioned polyethylene is formed, albeit in a rather slow reaction. A reasonable explanation of this effect is that a dissociation–association equilibrium between the phosphine-free and the P(*t*-C₄H₉)₃-modified catalyst exists, with polyethylene being formed as the product of the P(*t*-C₄H₉)₃-modified catalyst (51). [Changes in the optical yield on variation of the nickel:phosphine ratio in catalytic asymmetric synthesis with nickel catalysts (94, 95) have also been explained as the result of dissociation of bulky phosphine molecules from the catalyst.]

It is apparent that in the sequence of catalysts modified with phosphines shown in Table I, a gradual decrease in the relative rate constants for displacement vs. insertion (k_d/k_i) takes place; this is accompanied by a decrease in the activity of the catalyst. The order parallels the increasing steric demands rather than the basicity of the phosphines: $\text{P}(\text{CH}_3)_3$, for example, is a stronger base than $\text{P}(\text{C}_6\text{H}_5)_3$. However, systematic investigations of the origin of this effect are still lacking. The decrease of the k_d/k_i ratio can be explained on the basis of an increasing steric demand of the phosphine by assuming that the displacement reaction takes place via a penta- (or higher) coordinated nickel hydride intermediate having two olefin molecules simultaneously coordinated to the metal atom. The associative mechanism for exchange reactions involving square-planar d^8 complexes implies formation of a five-coordinate intermediate (96). It would be expected on the basis of this mechanism that with increasing size, the phosphine complexed to the nickel atom would suppress the formation of such higher-coordinated species, whereby the displacement step [Eq. (11b)] will be suppressed to a much larger extent than the insertion step [Eq. (11a)], because this step is associated with a decrease in coordination number.

C. Olefin Isomerization

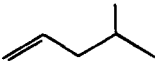
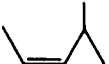
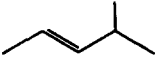
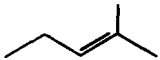
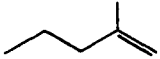
The observation that the k_d/k_i ratio can be varied by the choice of phosphine (Section IV,B) has practical consequences for the selectivity control in reactions involving olefins other than ethylene. Using a catalyst modified by $\text{P}(\text{CH}_3)_3$ (for which the displacement reaction is rapid and the value of k_d/k_i is high), rapid double-bond isomerizations without significant dimerization occurs (high selectivity of isomerization vs. dimerization). On the other hand, catalysts having a low k_d/k_i ratio are able to dimerize or oligomerize olefins or induce intramolecular carbon-carbon coupling reactions without extensive double-bond isomerization.

The influence of phosphines on the extent and rate of isomerization of propene dimers has been investigated at 0°C using catalysts prepared from π -allylnickel chloride, phosphine, and ethylaluminum dichloride in chlorobenzene (49, 51, 97). From these results, it is clear that the effectiveness of isomerization decreases in the order $\text{P}(\text{CH}_3)_3 > \text{P}(\text{C}_6\text{H}_5)_3 > \text{P}(\text{C}_2\text{H}_5)_3 \sim \text{P}(n\text{-C}_4\text{H}_9)_3 > \text{P}(i\text{-C}_3\text{H}_7)_3 \sim \text{P}(c\text{-C}_6\text{H}_{11})_3$ —in good agreement with that expected on the basis of decreasing k_d/k_i ratios. Isomerization of propene dimers is also possible with phosphine-free catalysts, but in this case the isomerization is accompanied by extensive oligomerization (51). The isomerization of propene dimers is of practical importance in

the separation of the mixtures produced by the nickel-catalyzed dimerization of propene (see Section IV,E). Using the $\text{P}(\text{CH}_3)_3$ - or $\text{P}(\text{C}_6\text{H}_5)_3$ -modified catalyst, it is possible to convert the propene dimers into a mixture consisting almost exclusively of 2-methyl-2-pentene and 2,3-dimethyl-2-butene, which can be subsequently separated by distillation.

In favorable cases for some single olefinic species, thermodynamic equilibria with respect to double-bond position can be attained at low temperatures without significant oligomerization. For example, *cis*-2-butene has been isomerized with the $\text{P}(\text{CH}_3)_3$ -modified catalyst at -20°C to give the thermodynamic equilibrium mixture having the composition 78.8% *trans*-2-butene, 19.5% *cis*-2-butene, and 1.7% 1-butene. The isomerization of 4-methyl-1-pentene (or of 2-methyl-1-pentene) in the presence of the same catalyst at 0°C also leads to the thermodynamic equilibrium mixture with the composition shown in Table II. If the reaction is carried out at low temperature, the individual isomerization steps can be followed: At -58°C , isomerization to *cis*-4-methyl-2-pentene occurs and is followed by isomerization to the *trans* isomer; this is then con-

TABLE II
ISOMERIZATION OF 4-METHYL-1-PENTENE AT $0^\circ\text{C}^{a,b}$

Olefin	Concentration (%)
	0.2
	0.9
	7.1-7.3
	83.6-84.0
	7.8-8.6

^a Catalyst: $\pi\text{-C}_3\text{H}_5\text{NiCl}[\text{P}(\text{CH}_3)_3]\text{-C}_2\text{H}_5\text{AlCl}_2$.

^b From Karmann (51).

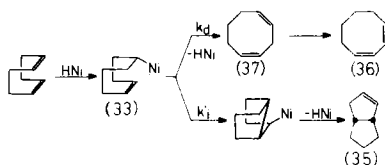
verted into 2-methyl-2-pentene at -40°C . By using catalysts of lower isomerization activity, the intermediates of the isomerization of 4-methyl-1-pentene to 2-methyl-2-pentene can be obtained in good yields. By carrying out the reaction at -58°C with a catalyst modified by $\text{P}(\text{c-C}_6\text{H}_{11})_3$, it is possible to enrich *cis*-4-methyl-2-pentene to 78% (conversion 85%), whereas the use of the phosphine-free catalyst at the same temperature and a conversion of 98.6% gives *trans*-4-methyl-2-pentene in 91% purity. Linear α -olefins, e.g., 1-hexene, can be isomerized using the $\text{P}(\text{CH}_3)_3$ -modified catalyst with fairly high selectivity to the corresponding β -olefins; in this way 1,7-octadiene has been isomerized at -40°C to a mixture containing 90% 2,6-octadienes. Isomerization of tri- or tetrasubstituted olefins (such as **17** and **18**) is possible using phosphine-free nickel catalysts (51).

A convincing example of selectivity control in isomerization reactions is the formation of *cis*-2-butene from the isomerization of 1-butene using the catalyst $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NiX}_2\text{-P}(\text{C}_6\text{H}_5)_3\text{-Zn-SnCl}_2$; a ratio of *cis*-2-butene:*trans*-2-butene as high as 98:2 has been observed. Isomerization to the thermodynamically more stable *trans*-olefin occurs only after conversion of all the 1-butene (98). Further examples of selective olefin isomerization will be discussed in Section IV,D.

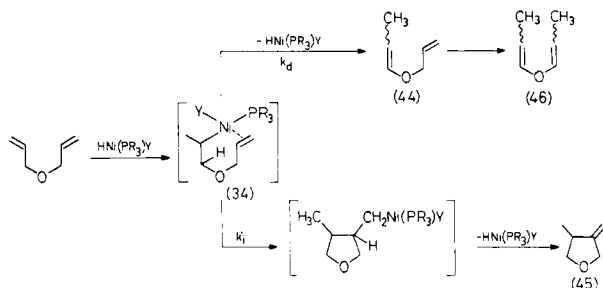
D. Reactions Involving 1,5- and 1,6-Dienes

Under the influence of nickel catalysts, 1,5- and 1,6-dienes undergo isomerization and cyclization, preferably to five-membered ring compounds. The cyclization takes place probably via an intramolecular insertion reaction (k_i) involving a π -5-alken-1-ynickel complex such as **33**, Table III, and **34**, Table IV formed by $\text{Ni} \rightarrow \text{C}_1$ and $\text{Ni} \rightarrow \text{C}_2$ additions

TABLE III
ISOMERIZATION OF 1,5-CYCLOOCTADIENE



	$\text{P}(\text{CH}_3)_3$	$\text{P}(\text{C}_6\text{H}_5)_3$	Phosphine-free catalyst
% 35	5.5	36	96
% (37 + 36)	93	62	Trace

TABLE IV
 ISOMERIZATION OF DIALLYL ETHER


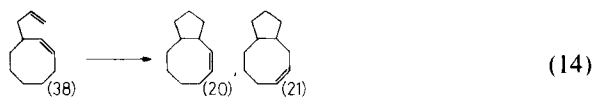
Y ⁻	PF ₆ ⁻	SbF ₆ ⁻	BF ₄ ⁻	ClO ₄ ⁻	CF ₃ SO ₃ ⁻	BF ₄ ⁻
PR ₃	P(i-C ₃ H ₇) ₃			P(CH ₃) ₃		P(CH ₃) ₃
% (46 + 44) / % 45	73/27	69/31	25/75	10/90	6/94	87/13

to a 1,5- or 1,6-diene. The nature and the distribution of the reaction products depends, among others, on the relative rates of the intramolecular insertion reaction (k_i) with respect to the rate of the displacement reaction (k_d) which leads to isomerization. Thus, the control of cyclization vs. double-bond isomerization of 1,5- and 1,6-dienes is a special case of dimerization vs. isomerization control. In fact, it has proved in several cases to be possible to control the cyclization/isomerization of 1,5- and 1,6-dienes, by varying the phosphine and the complex anion.

1. Phosphine Control

The phosphine dependence of isomerization vs. cyclization is found to be the same as that of dimerization vs. oligomerization (see Section IV, B): i.e., $P(CH_3)_3 > P(C_6H_5)_3 > \text{phosphine-free} > P(c-C_6H_{11})_3$. This is illustrated by the following examples. 1,5-Cyclooctadiene can be transformed in excellent yield into bicyclo[3.3.0]octene-2 (**35**) (Table III) by using the phosphine-free catalyst. The reaction course can be directed to almost complete formation of 1,3- and 1,4-cyclooctadiene (**36** and **37**) by employing the $P(CH_3)_3$ -modified catalyst (**99**, **100**). The double-bond isomerization occurs in a stepwise manner, and it is possible, by terminating the reaction before completion, to isolate 1,4-cyclooctadiene in up to 40% yield. With the $P(C_6H_5)_3$ -modified catalyst, isomerization and cyclization products in the ratio 3:2 are obtained. With other 1,5-dienes, such as 1,5-hexadiene, the yields of cyclization products using phosphine-free

catalysts are low—mainly 1,3- and 1,4-dienes are formed. In such cases it is possible to increase the yield of cyclic products by using catalysts modified with $P(c-C_6H_{11})_3$ or $P(i-C_3H_7)_3$; 3-allylcyclooctene (**38**) has thus been transformed in 35–40% yield into bicyclo[6.3.0]undecene-2 and -3 (**20** and **21**) [Eq. (14)] (**4**):

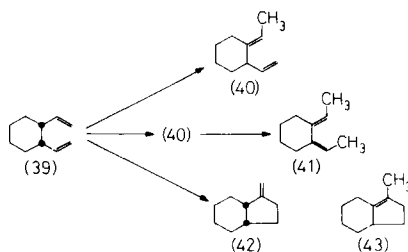


cis-1,2-Divinylcyclohexane (**39**) (Scheme 4) is isomerized by the phosphine-free catalyst to give a high yield of 1-vinyl-2-ethylidenecyclohexane (**40**); the use of the stronger isomerizing $P(CH_3)_3$ -modified catalyst leads to *Z,E*-1,2-diethylidenecyclohexane (**41**) as the main product, while with the $P(c-C_6H_{11})_3$ -modified catalyst the cyclic products **42** and **43** are mainly obtained (**99**).

2. Influence of the Anion

Catalysts prepared using aluminum halides or alkylaluminum halides as the Lewis acid have the disadvantage that they cannot be used in the presence of olefinic substrates containing functional groups such as ethers, because these destroy the complexes **3** or **4**. This difficulty has been overcome by using catalysts containing anions such as PF_6^- , SbF_6^- , BF_4^- , ClO_4^- , and $CF_3SO_3^-$ (**65**).

During the study of the isomerization of diallyl ether with catalysts of this type, it was observed that the nature of the complex anion (Y) has a profound influence on the relative rate of isomerization with respect to cyclization. Diallyl ether can be isomerized to a mixture consisting mainly of allyl propenyl ethers (**44**) with a small amount of 2-methyl-3-methylene-tetrahydrofuran (**45**) and dipropenyl ether (**46**); the catalyst for this



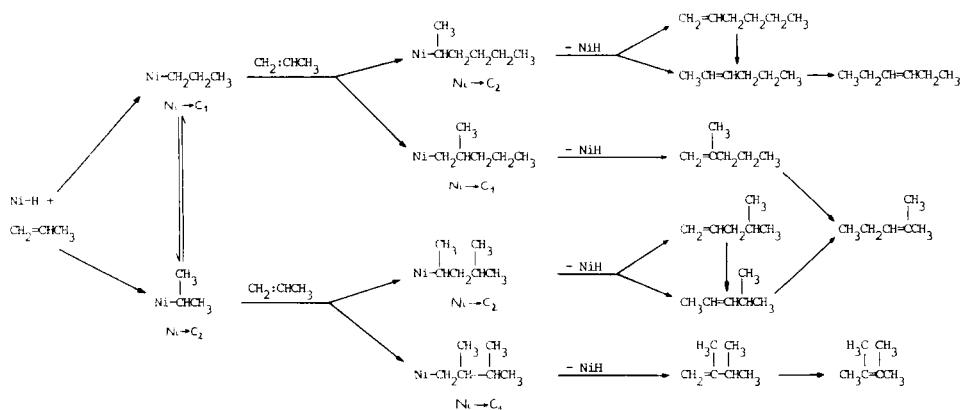
SCHEME 4

reaction is formed from π -allylnickel chloride, $P(CH_3)_3$, and silver tetrafluoroborate (Table IV). As shown in Table IV, both the phosphine and the anion component affect the proportion of the cyclic vs. open-chain isomerization products, and by a judicious choice of phosphine and anion it is possible to increase the yield of the cyclic product to 94%. With diallyl ether as substrate and using a $P(i-C_3H_7)_3$ -modified catalyst, the anions may be arranged in the following order of "increasing cyclization vs. isomerization selectivity": $PF_6^- \sim SbF_6^- < BF_4^- < ClO_4^- < CF_3SO_3^-$. The influence of the complex anion has also been studied for the cyclization of 1,6-heptadiene: again, the highest yield (70%) of the cyclic product, 1-methyl-2-methylenecyclopentane (**47**) (see Table X), was obtained using $CF_3SO_3^-$ as anion. The same catalyst modified with $P(i-C_3H_7)_3$ is able to convert 1,5-hexadiene to a mixture of methylenecyclopentane (81%), cyclohexene (16%), and 1,4-hexadiene (3%) (65). The use of the $P(i-C_3H_7)_3$ -modified nickel catalyst in conjunction with $CF_3SO_3^-$ as anion appears to be generally applicable for cyclization of 1,5- or 1,6-dienes.

E. The Dimerization of Propene

The dimerization of propene has been extensively studied because the propene dimers are of considerable interest as fuel additives and as starting materials for the preparation of monomers (4, 48, 49, 101). The reaction course can be controlled to give methylpentenes, 2,3-dimethylbutenes (2, 4, 7, 47, 51), or hexenes (44–46) as the main products.

In contrast to the examples of selectivity control discussed in the previous sections, the problem here is control of the *regioselectivity* of the individual reaction steps. This is evident from the Scheme 5. In the first reaction step the nickel-hydride species adds to propene forming a propyl- or isopropyl-nickel intermediate; this step is reversible, and the ratio of the two species can be controlled both thermodynamically and kinetically. In the second step, a second molecule of propene reacts to give four alkylnickel intermediates from which, after β -H elimination, 8 primary products are produced (Scheme 5). 2-Hexene and 4-methyl-2-pentene could be the products of either isomerization or the primary reaction. Isomerization leads to 3-hexene, 2-methyl-2-pentene (the common isomerization product of 2-methyl-1-pentene and 4-methyl-2-pentene), and 2,3-dimethyl-2-butene. It can be seen from the Scheme 5 that, if the isomerization to 2-methyl-2-pentene can be neglected, the distribution of the products enables an estimate to be made of the direction of



SCHEME 5

addition ($\text{Ni} \rightarrow \text{C}_1$ or $\text{Ni} \rightarrow \text{C}_2$) of the catalyst. The direction of addition in the first step may be defined by the quotient p , where

$$p = \frac{\%(\text{2-methyl-1-pentene} + \text{1- and 2-hexene})}{\%(\text{4-methyl-1- and 2-pentene} + \text{2,3-dimethylbutenes})}$$

while the *average* direction of addition in the second step is given by q , where

$$q = \frac{\%(\text{2-methyl-1-pentene} + \text{2,3-dimethylbutenes})}{\%(\text{4-methyl-1- and 2-pentene} + \text{1- and 2-hexene})}$$

The propyl-nickel/isopropyl-nickel proportion will be equal to p only if (a) the rate of formation of the individual propene dimers is proportional to the concentration of the corresponding alkyl-nickel intermediates, and (b) the reactivity of the propyl-nickel and isopropyl-nickel bond toward a further propene molecule is identical. The quotient q represents the average $\text{Ni} \rightarrow \text{C}_1/\text{Ni} \rightarrow \text{C}_2$ ratio in the second step as long as condition (a) is obeyed. According to kinetic measurements, the rate-determining step in the propene dimerization with nickel catalysts is the insertion of propene into the $\text{Ni}-\text{C}$ bond (42, 64) and not the β -H elimination: this naturally supports assumption (a). An independent indication of the validity of assumption (b) will be discussed below.

The influence of the phosphine on the composition of the propene dimers for a series of phosphines is given in Table V. From Table V it can be seen that the yield of hexenes and of methylpentenes decreases from 21.6 to 0.1% and from 73.9 to 19.0%, respectively, while at the same time the yield of 2,3-dimethylbutenes increases from 4.5 to 80.9%.

TABLE V
THE INFLUENCE OF PHOSPHINES ON THE NICKEL-CATALYZED DIMERIZATION OF
PROPENE^{a,b}

Phosphine	Σn -Hexene	Σ Methylpentene	Σ 2,3-Dimethylbutene
—	19.8	76.0	4.2
P(C ₆ H ₅) ₃	21.6	73.9	4.5
(C ₆ H ₅) ₂ PCH ₂ P(C ₆ H ₅) ₂	12.2	83.0	4.7
(C ₆ H ₅) ₂ PCH ₂ C ₆ H ₅	19.2	75.4	5.1
(C ₆ H ₅) ₂ P(CH ₂) ₃ P(C ₆ H ₅) ₂	20.1	73.3	6.6
P(CH ₃) ₃	9.9	80.3	9.8
(C ₆ H ₅) ₂ P- <i>i</i> -C ₃ H ₇	14.4	73.0	12.6
P(C ₂ H ₅) ₃	9.2	69.7	21.1
P(C ₄ H ₉) ₃	7.1	69.6	23.3
P(CH ₂ C ₆ H ₅) ₃	6.7	63.6	29.2
(cyclo-C ₆ H ₁₁) ₂ P—P— (cyclo-C ₆ H ₁₁) ₂	4.4	46.5	49.2
P(cyclo-C ₆ H ₁₁) ₃	3.3	37.9	58.8
P(<i>i</i> -C ₃ H ₇) ₃	1.8	30.3	67.9
(<i>t</i> -C ₄ H ₉) ₂ PCH ₃	1.2	24.5	74.0
(<i>t</i> -C ₄ H ₉) ₂ PCH ₂ CH ₃	0.6	22.3	77.0
(<i>i</i> -C ₃ H ₇) ₂ P- <i>t</i> -C ₄ H ₉	0.1	19.0	80.9
(<i>t</i> -C ₄ H ₉) ₂ P- <i>i</i> -C ₃ H ₇	0.6	70.1	29.1

^a Catalyst: (π -C₃H₅NiX)₂-(C₂H₅)₃Al₂Cl₃-Ligand; -20°C; 1 atm.

^b From Bogdanović *et al.* (4) and Karmann (51).

The composition of the dimer obtained using the phosphine-free catalyst is close to that obtained with the P(C₆H₅)₃-modified catalyst. Substitution of (*i*-C₃H₇)₂P-*t*-C₄H₉ by (*t*-C₄H₉)₂P-*i*-C₃H₇ leads to a decrease in the yield of 2,3-dimethylbutene from 80.9 to 29.1%.

A better insight into the effect of the phosphine is obtained from studying the quotients *p* and *q* (Table VI), which reflect the direction of addition in the first and second reaction steps. From the results shown in Table VI it can be seen that, with exception of (*t*-C₄H₉)₂P-*i*-C₃H₇, the changes in the composition of the propene dimers are mainly associated with changes in the second step, from predominantly Ni → C₂ addition (*q* = 18:82) to a highly selective Ni → C₁ addition (*q* = 98:2). For a large number of phosphines, in the first step the nickel hydride species adds to propene in a manner largely independent of the nature of the phosphine—with predominant Ni → C₂ addition.

An exception is the increase in the yield of methylpentene and the decrease in the yield of 2,3-dimethylbutene observed on substituting (*i*-C₃H₇)₂P-*t*-C₄H₉ by (*t*-C₄H₉)₂P-*i*-C₃H₇; this is apparently due to a change

TABLE VI
THE INFLUENCE OF PHOSPHINES ON THE DIRECTION OF ADDITION DURING
PROPENE DIMERIZATION^a

Phosphine	<i>p</i>	<i>q</i>
P(C ₆ H ₅) ₃	25:75	18:82
(C ₆ H ₅) ₂ PCH ₂ P(C ₆ H ₅) ₂	21:79	13:87
(C ₆ H ₅) ₂ PCH ₂ C ₆ H ₅	27:73	13:87
(C ₆ H ₅) ₂ P(CH ₂) ₃ P(C ₆ H ₅) ₂	24:76	10:90
P(CH ₃) ₃	15:85	15:85
(C ₆ H ₅) ₂ P- <i>i</i> -C ₃ H ₇	29:71	27:73
P(C ₂ H ₅) ₃	17:83	29:71
P(C ₄ H ₉) ₃	18:82	34:66
P(CH ₂ C ₆ H ₅) ₃	22:78	45:55
(cyclo-C ₆ H ₁₁) ₂ PP(cyclo-C ₆ H ₁₁) ₂	18:82	62:38
P(cyclo-C ₆ H ₁₁) ₃	26:74	83:17
P(<i>i</i> -C ₃ H ₇) ₃	20:80	86:14
(<i>t</i> -C ₄ H ₉) ₂ PCH ₃	12:88	85:15
(<i>t</i> -C ₄ H ₉) ₂ PC ₂ H ₅	20:80	97: 3
(<i>i</i> -C ₃ H ₇) ₂ P- <i>t</i> -C ₄ H ₉	15:85	97: 3
(<i>t</i> -C ₄ H ₉) ₂ P- <i>i</i> -C ₃ H ₇	69:31	98: 2

^a Taken from Karmann (51).

in the direction of addition in the first reaction step from predominantly Ni → C₂ addition to predominantly Ni → C₁ addition.

Further examples which show that the direction of Ni—C addition to propene can be changed from Ni → C₂ to Ni → C₁ by introducing P(*i*-C₃H₇)₃ are to be found in the codimerizations of ethylene with propene (4, 12, 29) and of 1,3-cyclooctadiene with propene (4, 79). The last example is particularly informative, for in this case no ambiguity as to the assignment of the products to Ni → C₁ or Ni → C₂ type addition exists.

An important contribution to an understanding of the mechanism of propene dimerization has been obtained by studying the reaction of nickel-hydride model complexes (85). The formation of the propyl- and isopropyl-nickel complexes **48** and **49** has been observed in the reactions of HNi(PR₃)Cl complexes (**50**) with propene at -78°C [Eq. (15)]:

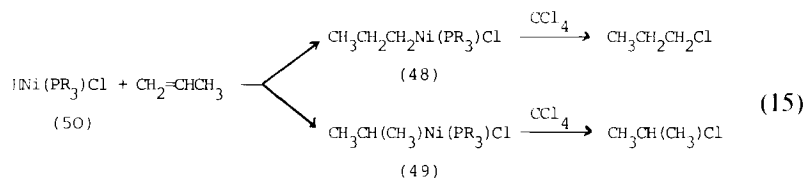


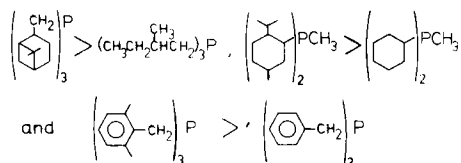
TABLE VII
ADDITION OF $\text{HNiX} [\text{PR}_3]$ TO $\text{CH}_3\text{CH}:\text{CH}_2^a$

Catalytic results (4, 51)			Model system (85)		
Ligand	$\begin{array}{c} \text{C} \\ \\ \text{Ni}-\text{C}-\text{C} \end{array}$	$\text{Ni}-\text{C}-\text{C}-\text{C}$	Ligand	$\begin{array}{c} \text{C} \\ \\ \text{Ni}-\text{C}-\text{C} \end{array}$	$\text{Ni}-\text{C}-\text{C}-\text{C}$
$\text{P}(\text{C}_2\text{H}_5)_3$	83%	17%	$\text{P}(\text{OC}_6\text{H}_5)_3$	82%	18%
$\text{P}(\text{cyclo}-\text{C}_6\text{H}_{11})_3$	74%	26%	$\text{P}(\text{cyclo}-\text{C}_6\text{H}_{11})_3$	80%	20%
$\text{P}(t\text{-C}_4\text{H}_9)_2\text{-i-C}_3\text{H}_7$	31%	69%	$\text{P}(t\text{-C}_4\text{H}_9)_2\text{-i-C}_3\text{H}_7$	19%	81%

^a From Bogdanović *et al.* (4, 51) and Bönemann *et al.* (85).

The ratio of the nickel-propyl species **48** and **49** was determined by adding CCl_4 and estimating the ratio of *n*-propylchloride to isopropylchloride. The results are shown in Table VII. The proportion *n*-propyl-/isopropyl-nickel of 20/80 is independent of the basicity of the ligand and is reversed by the sterically demanding ligand $(t\text{-C}_4\text{H}_9)_2\text{P-i-C}_3\text{H}_7$, in striking agreement with the results obtained from the dimerization of propene.

Systematic investigations have shown that the effect of phosphines on the direction of Ni—C and Ni—H addition to propene has largely a steric origin (51, 102). This conclusion is drawn by a study of the effect of phosphines having different donor-acceptor properties and similar steric properties and phosphines having different steric and similar donor-acceptor properties. For example, in the series *ortho*-, *meta*-, and *para*-substituted triphenylphosphines, an increase in 2,3-dimethylbutene and a decrease in hexene yield is observed only for the *ortho*-substituted triphenylphosphine. Among aliphatic phosphines of comparable basicity, higher *q* values (see above) are observed with those phosphines having larger organic groups, for example

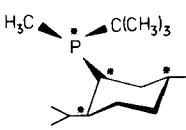
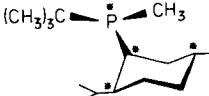


A convincing example of the operation of steric effects is to be seen in the difference in the composition of propene dimers obtained using epimers of menthyl(*t*-C₄H₉)PCH₃ (Table VIII) with opposite configuration at the phosphorous atom (103).

From the results discussed above, it appears that the main influence of phosphines in controlling the course of propene dimerization consists in hindering, through steric interference, the second insertion step from proceeding according to Ni → C₂ type addition. An explanation for the predominant Ni → C₂ type addition in the absence of steric hindrance in terms of the polarity of metal-carbon, metal-H, and C=C bonds has been recently presented (104). The extremely bulky phosphine $(t\text{-C}_4\text{H}_9)_2\text{P-i-C}_3\text{H}_7$ is even able to reverse the direction of Ni—H addition to propene, a step which is obviously less sensitive toward steric hindrance.

The isopropyl-/*n*-propyl-nickel ratio of ~80/20 observed for the majority of phosphines limits the yield of 2,3-dimethylbutene to 80–85%. Higher yields can be achieved only if the selectivity toward Ni → C₂ addition in the first step can be further increased. One such possibility is the use of a catalyst modified with $(i\text{-C}_3\text{H}_7)_2\text{P-}t\text{-C}_4\text{H}_9$ at low temperature

TABLE VIII
INFLUENCE OF EPIMERS OF MENTHYL-*tert*-BUTYLMETHYLPHOSPHINE ON THE
COMPOSITION OF PROPENE DIMERS^a

Ligand	Epimer Ratio	Composition of propene dimers (%)		
		C—C—C—C—C—C	$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \end{array}$	$\begin{array}{cc} \text{C} & \text{C} \\ & \\ \text{C}-\text{C} & -\text{C}-\text{C} \end{array}$
	93:7	2.3	36.7	61.0
	17:83	2.3	51.8	45.5

^a Catalyst: $\pi\text{-C}_3\text{H}_5\text{Ni}(\text{L})\text{Cl}\cdot\text{Et}_3\text{Al}_2\text{Cl}_3$; -20°C .

(Table IX). With this catalyst, lowering the reaction temperature from -20° to -60°C results in an increase in the yield of 2,3-dimethylbutene in the dimer fraction from 80.9 to 96.3%. With the $\text{P}(\text{i-C}_3\text{H}_7)_3$ -modified catalyst, no such pronounced temperature effect is observed (80).

F. Enantioselectivity Control

The recognition that the course of nickel-catalyzed olefin oligomerization reactions is extremely sensitive to small changes in the phosphine structure led to the discovery that these catalysts, in combination with optically active phosphines, can be employed in catalytic asymmetric synthesis (79, 94, 95, 105, 106) [for a review, see Bogdanović *et al.* (107)]. The most effective phosphines have been found to be those containing a menthyl group, e.g., (–)-dimenthylmethylphosphine or (–)-dimenthylisopropylphosphine, and the most successful syntheses involve the co-dimerization of ethylene with a cyclic olefin, e.g., ethylene with norbornene to give optically active *exo*-2-vinylnorbornene (**51**) [Eq. (16)]. The e.e. of **51** increases on lowering the reaction temperature, and a value of 80% is obtained at -97°C . From the relationship between the optical

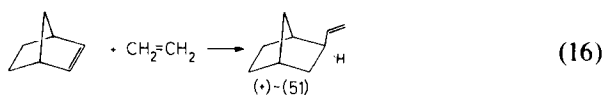


TABLE IX
 INFLUENCE OF TEMPERATURE ON THE COMPOSITION OF PROPENE DIMERS^a

Ligand	Temperature °C	Composition of propene dimers (%)		
		C—C—C—C—C—C	C C—C—C—C—C	C C C—C—C—C
(i-C ₃ H ₇) ₂ P- <i>t</i> -C ₄ H ₉	+20	3.8	35.6	60.6
	0	1.3	23.0	75.7
	-20	0.1	19.0	80.9
	-40	0.2	10.0	89.8
	-60	0.2	3.5	96.3
P(i-C ₃ H ₇) ₃	-20	1.8	20.8	77.0
	-60	0.7	19.6	79.6

^a Catalyst: (π -C₃H₅NiCl)₂-C₂H₅AlCl₂-Ligand; reaction rate: 3-6 kg product/g Ni·hour; C₉ and higher oligomers: 10-20%.

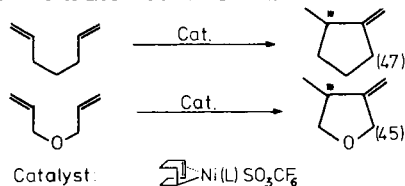
yield and reaction temperature, a $\Delta\Delta E^\ddagger$ difference between (+)- and (-)- **51** of 1.5 kcal/mole has been estimated.

The favorable influence of lowering the reaction temperature on the optical yield is apparently general for asymmetric olefin oligomerization. The high optical purity is, in part, a result of the high activity of the nickel catalyst which enables the codimerization reactions to be carried out under very mild conditions, thereby allowing full implementation of the small differences in the free activation enthalpy for formation of the diastereoisomeric intermediates. It can be speculated that in order to obtain high optical yields at higher temperatures, the catalyst system, and in particular the phosphine component, will have to be made more rigid.

In one example of an asymmetric codimerization, a pronounced effect on the optical yield has been observed by increasing the phosphine/nickel molar ratio (94, 95). This effect may be ascribed to suppression of a dissociation process or to complexation of a second molecule of the inducing phosphine to the nickel atom.

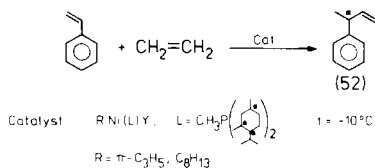
Asymmetric cyclizations of 1,6-heptadiene and of diallyl ether have been studied under the influence of a catalyst modified with menthyl(*t*-C₄H₉)PCH₃—a phosphine having chiral centers both at phosphorus and at one of the organic groups. Catalytic reactions have been performed using the epimers in a proportion of 93:7 and 17:83, respectively (Table X) (103). In this case, the inversion of the configuration at the phosphorus atom has a strong influence on the optical yield, suggesting that

TABLE X
ASYMMETRIC CYCLIZATIONS OF 1,6-HEPTADIENE AND OF DIALLYL ETHER USING
CATALYST MODIFIED WITH EPIMERS OF MENTHYL-*tert*-BUTYLMETHYLPHOSPHINE



Ligand	Temperature (°C)	Epimer ratio	Substrate	Optical yield	
				(Obs.) (%)	(Calc.) (%)
	+ 5	93:7		(-) 1.6	(-) 1.4
	+ 5	17:83		(-) 27.8	(-) 33.2
	-30	93:7		(-) 14.9	(-) 13.0
	-30	17:83		(-) 36.9	(-) 41.7
	0	93:7		(-) 0.7	(-) 0.5
	0	17:83		(-) 13.2	(-) 16.0

TABLE XI
ASYMMETRIC CODIMERIZATION OF STYRENE
WITH ETHYLENE; INFLUENCE OF THE COMPLEX
ANION OF THE CATALYST ON OPTICAL YIELD



Y^-	Absolute configuration	Optical yield (%)
SbF_6^-	(+)-S	37
PF_6^-	(+)-S	33
$\text{Al}_2\text{Cl}_4(\text{C}_2\text{H}_5)_3^-$	(+)-S	31
BF_4^-	(+)-S	31
CF_3SO_3^-	(+)-S	16
ClO_4^-	(-)-R	12

both the chiral center at phosphorus and the chiral menthyl group determine the asymmetric induction.

Finally, in the codimerization of styrene with ethylene to optically active 3-phenyl-1-butene (**52**) (Table XI), it has been shown that the complex anion (Y) can exert a strong influence on the optical yield (103, 105).

No general trends, comparable to phosphine influence on regioselectivity, isomerization rate, etc. have as yet appeared from the investigations of the influence of different parameters on the optical yield in catalytic asymmetric syntheses, with the exception of the favorable influence of decreasing the reaction temperature. The search for enantioselective catalysts is likely to remain a matter of empiricism for some considerable length of time.

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It is a great pleasure for me to acknowledge the contribution of all the co-workers cited in the references. I would also like to thank my colleague P. W. Jolly for valuable comments.

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Palladium-Catalyzed Reactions of Butadiene and Isoprene

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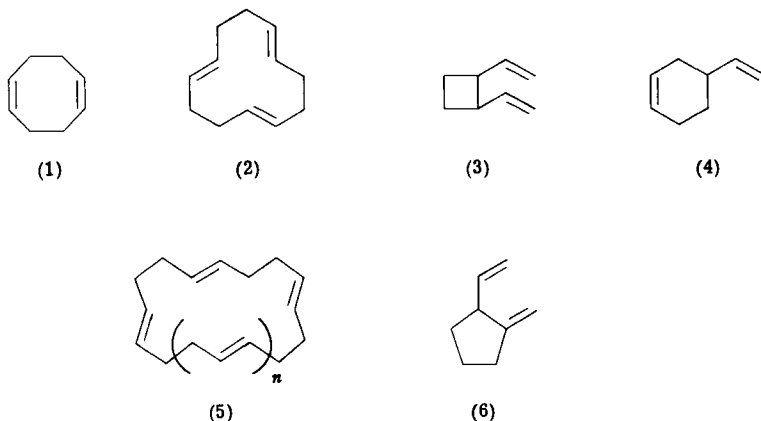
COMPARISON OF NICKEL- AND PALLADIUM-CATALYZED REACTIONS OF BUTADIENE

Reactions of conjugated 1,3-dienes, mainly butadiene and isoprene, catalyzed by transition metal complexes to form a number of linear and cyclic oligomers and telomers, are one of the most fascinating fields of research in the last 20 years. Extensive studies from academic and in-

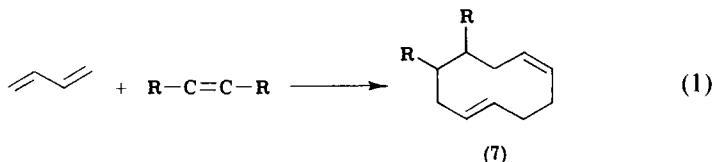
dustrial viewpoints have been carried out. Three types of reactions of conjugated dienes catalyzed by transition metal complexes are now known. They are (a) polymerization, (b) cyclization, and (c) linear oligomerization or telomerization.

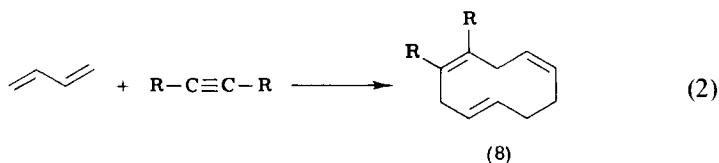
Polybutadiene and polyisoprene are produced and used mainly as synthetic rubber on an industrial scale by using transition metal catalysts, especially titanium- and nickel-based ones. By contrast, only minor attention has been paid to the palladium-catalyzed polymerization of butadiene. A mixture of 1,2-polybutadiene and *trans*- and *cis*-1,4-polybutadiene was obtained by using PdCl_2 as a catalyst (1, 2).

Among transition metal complexes used as catalysts for reactions of the above-mentioned types b and c, the most versatile are nickel complexes. The characteristic reactions of butadiene catalyzed by nickel complexes are cyclizations. Formations of 1,5-cyclooctadiene (COD) (1) and 1,5,9-cyclododecatriene (CDT) (2) are typical reactions (3-9). In addition, other cyclic compounds (3-6) shown below are formed by nickel catalysts. Considerable selectivity to form one of these cyclic oligomers as a main product by modification of the catalytic species with different phosphine or phosphite as ligands has been observed (3, 4).

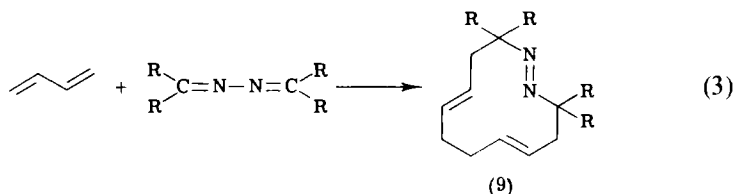


Also, cocyclizations of butadiene with olefins and acetylenes are possible to form the 10-membered rings 7 and 8 (10):

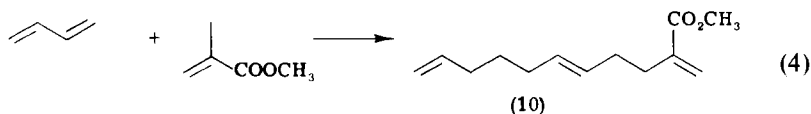




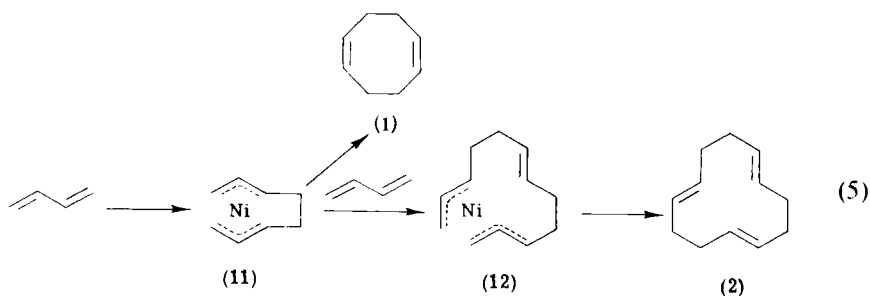
Furthermore, azines as a diene system were used for cocyclization with butadiene to form 12-membered heterocyclic compounds as **9** (11):



Linear oligomerization and telomerization of butadiene take place with nickel complexes in the presence of a proton source (7). In addition, cooligomerization of butadiene with functionalized olefins such as methacrylate is catalyzed by nickel complexes [Eq. (4)] (12, 13):

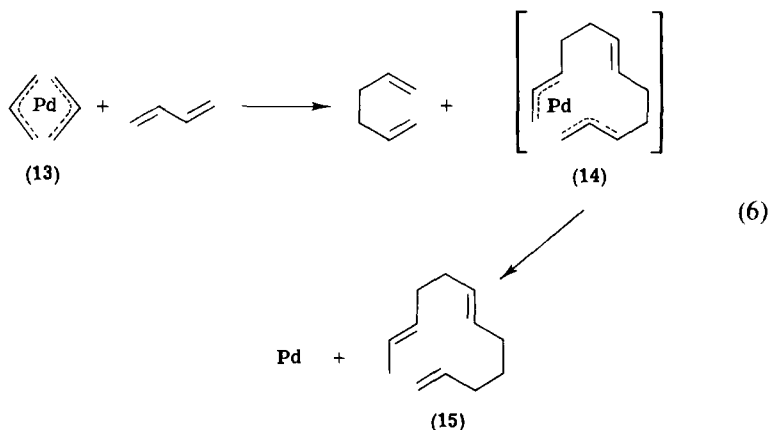


Mechanistic studies of the nickel-catalyzed cyclization of butadiene have been carried out. The formation of various cyclic compounds catalyzed by nickel complexes is explained via the intermediacy of π -allylic nickel complexes **11** and **12**.



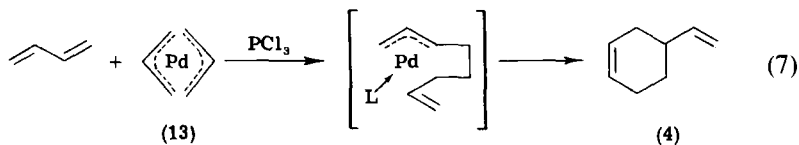
Similar studies on the reactions of butadiene and bis(π -allyl)palladium were carried out by Wilke and co-workers (4). Unlike the reactions with nickel complexes, no cyclization took place, and 1,6,10-dodecatriene

(15) was obtained by the reaction of bis(π -allyl)palladium (13) with butadiene, presumably via the formation of an intermediate complex (14). Although nickel and palladium form the complexes of the same type 12 and 14, no cyclization takes place with palladium.



Wilke explained this result by considering the difference in atomic volumes of palladium and nickel. A strong affinity of palladium with hydrogen to form palladium hydride by the abstraction of hydrogen from a coordinated carbon chain, and subsequent intermolecular hydrogen shift, are other factors contributing to the preferential formation of linear oligomers with palladium catalysts. No hydrogen shift takes place in the cyclization reactions.

Next, the effect of ligand of palladium complex on the reaction of butadiene was studied. Only vinylcyclohexene (4) was obtained by the reaction of butadiene at 90°C using bis(π -allyl)palladium (13) and trichlorophosphine (1:1).

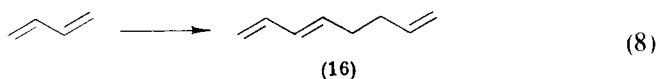


After that, studies on the palladium-catalyzed reactions of conjugated dienes attracted little attention. They have only been reexamined since the late 1960's. The scope of the reaction of butadiene catalyzed by palladium complexes has gradually been established. The catalysis by palladium is different from those of other transition metals. Although palladium is located below nickel in the periodic table, the catalytic

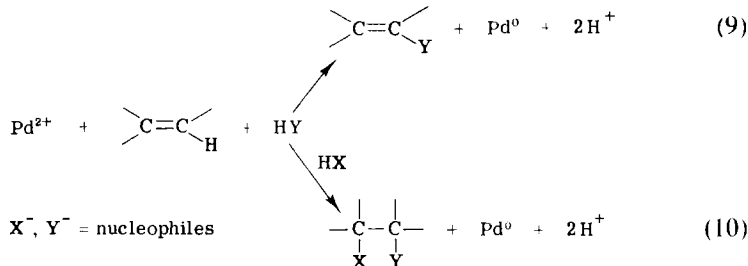
properties of palladium are unique and quite different from those of nickel. Reviews of the palladium-catalyzed reaction of butadiene have been published (8, 9, 14). In this review, a general survey of the reactions of butadiene and isoprene in the presence of palladium catalysts is given; also, related reactions catalyzed by nickel complexes are treated briefly for comparison.

Unlike nickel catalysts, palladium catalysts undergo neither cyclodimerization nor cyclotrimerization to form COD or CDT. Only one paper by Chepaikin and Khidekel reported that a mixture of divinylcyclobutanes was obtained from butadiene using palladium salts with noncomplexing anions such as perchlorate and boron tetrafluoride (15). This is a big difference between the catalyses of palladium and nickel.

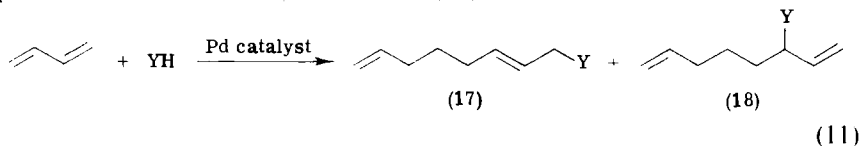
There are two main types of reactions of conjugated dienes catalyzed by palladium complexes. The first type is the linear dimerization to form 1,3,7-octatriene (**16**) in the absence of a nucleophile:



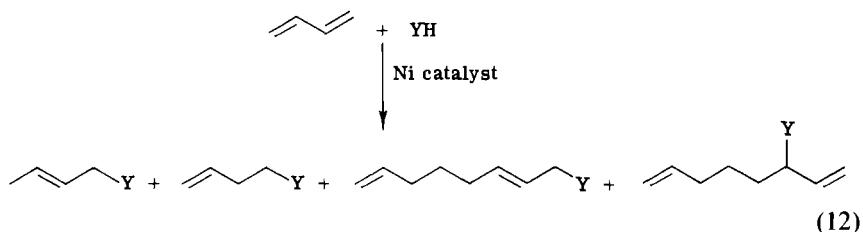
The most characteristic and useful reaction is the dimerization with incorporation of certain nucleophiles. It is well-known that simple olefins coordinated by Pd^{2+} compounds undergo nucleophilic substitutions [Eq. (9)] or addition reactions [Eq. (10)] (16, 17). Water, alcohols, and carboxylic acids are typical nucleophiles which attack olefins to form aldehydes, ketones, vinyl ethers, and vinyl esters.



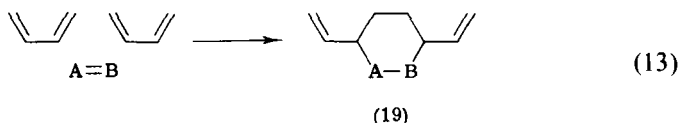
Similar nucleophiles have been found to react with butadiene to form dimeric telomers in which nucleophiles are introduced mainly at the terminal position to form 8-substituted 1,6-octadiene (**17**). As a minor product, 3-substituted 1,7-octadiene (**18**) is formed:



These telomerization reactions of butadiene with nucleophiles are also catalyzed by nickel complexes. For example, amines (18–23), active methylene compounds (23, 24), alcohols (25, 26), and phenol (27) react with butadiene. However, the selectivity and catalytic activity of nickel catalysts are lower than those of palladium catalysts. In addition, a mixture of monomeric and dimeric telomers is usually formed with nickel catalysts:



The second characteristic reaction catalyzed by palladium catalysts is cocyclization of butadiene with the C=O bonds of aldehydes and the C=N bonds of isocyanates and Schiff bases to form six-membered heterocyclic compounds (19) with two vinyl groups, as expressed by the following general scheme:



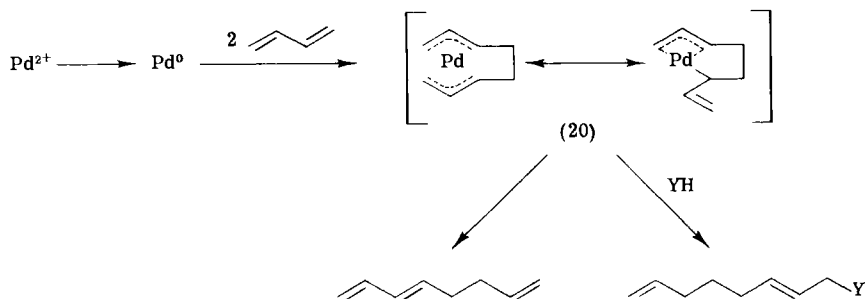
These cocyclization reactions of butadiene are possible only with palladium catalysts.

II

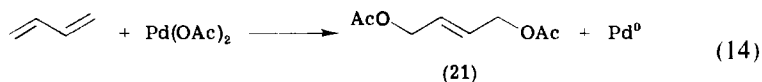
CATALYTIC SPECIES

It is apparent from mechanistic considerations that an active species in the palladium-catalyzed dimerization of butadiene is a zero-valent palladium complex, which forms bis- π -allylic complex **20**.

At first Smutny carried out the palladium-catalyzed reaction of butadiene with phenol using PdCl_2 as a catalyst (28, 29). Phenoxybutene and *o*- and *p*-butenylphenols were obtained in low conversion and yield. When pyridine was added, 8-phenoxy-1,6-octadiene was obtained in low yield. However, 8-phenoxy-1,6-octadiene and 3-phenoxy-1,7-octadiene



were obtained in high conversion when PdCl_2 was used as the catalyst with sodium phenoxide. It was later found that the catalytic activity of palladium can be greatly increased by using PPh_3 as a ligand. Hagihara and co-workers carried out efficient dimerization and telomerization of butadiene by using zero-valent palladium complexes as catalysts (30, 31). $\text{Pd}(\text{PPh}_3)_4$ [or, better, $\text{Pd}(\text{PPh}_3)_2$] coordinated by dienophiles, such as maleic anhydride or benzoquinone, was used. Furthermore, it became apparent that not only the zero-valent palladium complexes, but certain bivalent palladium compounds, can be used as active catalysts with combination of PPh_3 . Instead of the zero-valent palladium complexes, which are somewhat tedious to prepare and unstable in the air, easily available and stable bivalent palladium compounds such as $\text{Pd}(\text{OAc})_2$ are used with PPh_3 . Palladium acetylacetonate $[\text{Pd}(\text{acac})_2]$ is also suitable. These palladium compounds, used with PPh_3 , are reduced *in situ* to the zero-valent state which is stabilized by coordination of PPh_3 , they then act as true catalysts. For example, $\text{Pd}(\text{OAc})_2$ reacts oxidatively with stoichiometric amounts of butadiene to form diacetoxybutene (21) and zero-valent palladium. Therefore, in most cases, it is convenient to use $\text{Pd}(\text{OAc})_2$ and PPh_3 as the catalyst system for the dimerization of butadiene.



Another easily available palladium compound is PdCl_2 ; however, it has low or no activity. The chloride ion in the coordination sphere of palladium seems to inhibit the coordination of two moles of butadiene to form the bis- π -allylic complex. However, PdCl_2 can be used in the presence of an excess of bases, such as KOH, NaOH, sodium phenoxide, sodium acetate, potassium acetate, sodium methoxide, or tertiary amines. These bases deprive the chloride ion from the coordination sphere of palladium to form the active species. Thus, very stable and easily prepared

$\text{PdCl}_2(\text{PPh}_3)_2$ can be used as the catalyst with an excess of these bases. π -Allylpalladium nitrate, sulfate, and fluoride seem to be active catalysts (32).

It should be mentioned here that expensive palladium complexes used as catalysts must be recovered in any large-scale production of telomers. For this purpose, the palladium catalyst remaining in the reaction mixture can be converted into stable and difficultly soluble $\text{PdCl}_2(\text{PPh}_3)_2$ by treatment with hydrogen chloride and PPh_3 . The precipitated $\text{PdCl}_2(\text{PPh}_3)_2$ can be recovered and recycled with bases for a next run.

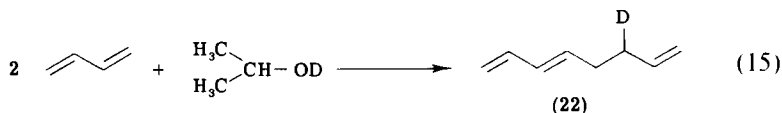
The presence of PPh_3 or other ligands is essential for high catalytic activity. Easily available PPh_3 is satisfactory in most cases. There are a number of papers reporting different catalytic properties observed by using different phosphines or phosphites as the ligand. Examples will be given in latter sections of this chapter. In most cases, however, PPh_3 is a satisfactory choice as the ligand.

III

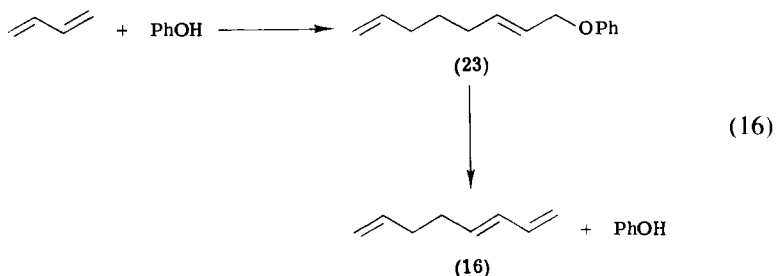
DIMERIZATION OF BUTADIENE

Butadiene is converted into 1,3,7-octatriene (**16**) when heated at 100°–120°C in aprotic solvents in the presence of a palladium catalyst. As the catalyst, $\text{Pd}(\text{PPh}_3)_2$ coordinated by maleic anhydride and benzoquinone is used (30, 31). $\text{Pd}(\text{PPh}_3)_4$ can be used, but it is less effective than the coordinatively unsaturated bisphosphine complex. As the aprotic solvents, benzene, tetrahydrofuran (THF), and acetone are used. Some protic solvents react with butadiene and cannot be used. Takahashi, Shibano, and Hagihara observed that the dimerization to give 1,3,7-octatriene proceeded more smoothly in isopropyl alcohol than in aprotic solvents (31). For example, the reaction in benzene at 100°C for 7 hours gave the triene in 23% yield, while the reaction in isopropyl alcohol at the same temperature for 4 hours produced the triene in 75% yield. Obviously, the formation of 1,3,7-octatriene involves hydrogen migration during the reaction. Accordingly, the increasing rate of the dimerization reaction in isopropyl alcohol in comparison with the reaction in the aprotic solvents suggests the participation of proton of the alcohol. In order to prove this speculation, the reaction of butadiene was carried out in deuterated isopropyl alcohol $(\text{CH}_3)_2\text{CHOD}$ (70% purity). The reaction product consisted of 1,3,7-octatriene (40%) and monodeuterated octatriene, **22** (60%). The deuteration probably took place at carbon 6 of the triene. It is reasonable that the addition of the proton from isopropyl

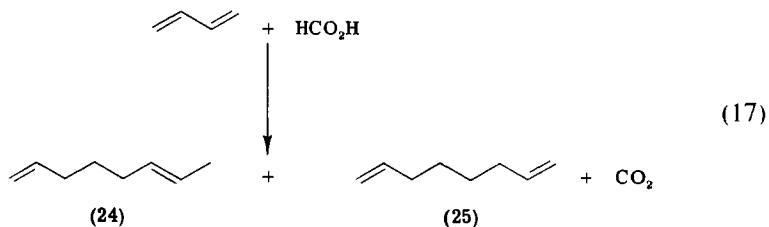
alcohol to carbon 6 and the elimination of the proton from carbon 4 result in an increasing rate of the hydrogen migration from carbon 4 to carbon 6.



Another way to prepare 1,3,7-octatriene is to eliminate phenol from 8-phenoxy-1,6-octadiene (**23**) by heating in the presence of palladium and PPh_3 (**28**):



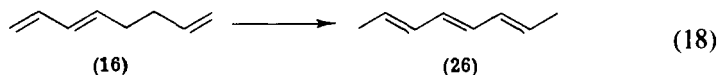
A different dimerization takes place in formic acid (**33**, **34**). Unlike other carboxylic acids which behave as nucleophiles, formic acid behaves as a reductant and the dimerization proceeds with partial reduction. By carrying out the reaction in a mixture of formic acid and triethylamine at 59°C using $\text{Pd}(\text{OAc})_2$, 1,6-octadiene (**24**) was obtained.



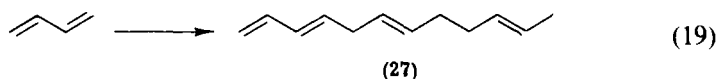
When PPh_3 was added, a mixture of 1,7-octadiene (**25**) and 1,6-octadiene (**24**) was obtained (**33**). 1,7-Octadiene was obtained in 80% selectivity by using $\text{PdCl}_2(\text{PPh}_3)_2$ and sodium propoxide as the catalyst system (**34**).

Kohnle, Slaugh, and Nakamaye reported that carbon dioxide greatly affects the catalytic activity of $\text{Pd}(\text{PPh}_3)_4$ and $\text{Pt}(\text{PPh}_3)_4$ in the reaction of butadiene to give 1,3,7-octatriene. Surprisingly, in the absence of carbon dioxide, vinylcyclohexene was formed (**35**). Musco and Silvani found

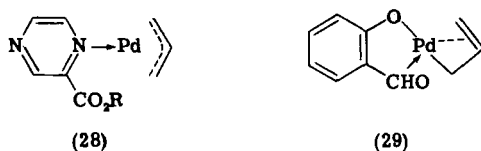
that PdL_n complexes ($\text{L} = \text{PPh}_3, \text{PEt}_3; n = 2, 3$) catalyze both the conversion of butadiene to 1,3,7-octatriene and its isomerization to 2,4,6-octatriene (**26**) in the presence of carbon dioxide (**36**).



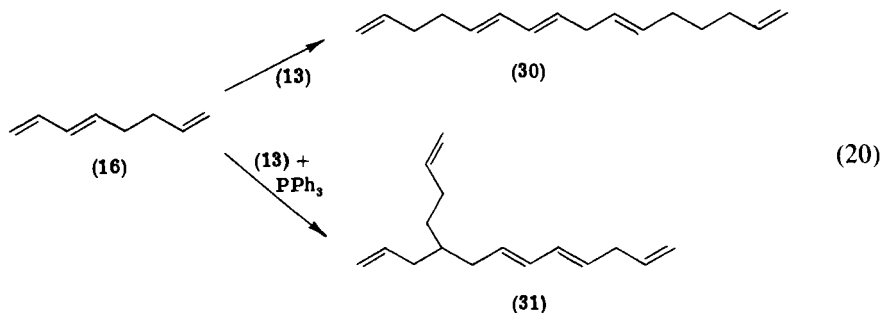
The main path of the palladium-catalyzed reaction of butadiene is the dimerization. However, the trimerization to form *n*-1,3,6,10-dodecatetraene takes place with certain palladium complexes in the absence of a phosphine ligand. Medema and van Helden observed, while studying the insertion reaction of butadiene to π -allylpalladium chloride and acetate (**32, 37**), that the reaction of butadiene in benzene solution at 50°C using π -allylpalladium acetate as a catalyst yielded *n*-1,3,6,10-dodecatetraene (**27**) with a selectivity of 79% at a conversion of 30% based on butadiene in 22 hours.



Also, the trimerization reaction was observed by using π -allyl complexes of palladium stabilized by chelating ligands, such as **28** and **29** (**38**). The reaction was carried out at 70°C in dimethylformamide (DMF) or dimethyl sulfoxide (DMSO), and 1,3,6,10-dodecatetraene (**27**) was obtained in 60% yield at 30% conversion.



1,3,7-Octatriene was converted into *n*-1,5,7,10,15-hexadecapentaene (**30**) with 70% selectivity by catalytic action of bis(π -allyl)palladium (**13**). On the other hand, 4-(3-butenyl)-1,6,8,11-dodecatetraene (**31**) was formed as a main product when PPh_3 was added in 1:1 ratio (**39**).



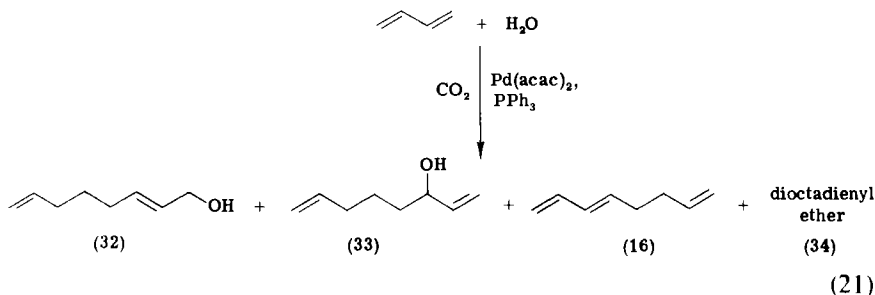
IV

TELOMERIZATION OF BUTADIENE

The most characteristic reaction of butadiene catalyzed by palladium catalysts is the dimerization with incorporation of various nucleophiles [Eq. (11)]. The main product of this telomerization reaction is the 8-substituted 1,6-octadiene, **17**. Also, 3-substituted 1,7-octadiene, **18**, is formed as a minor product. So far, the following nucleophiles are known to react with butadiene to form corresponding telomers: water, carboxylic acids, primary and secondary alcohols, phenols, ammonia, primary and secondary amines, enamines, active methylene compounds activated by two electron-attracting groups, and nitroalkanes. Some of these nucleophiles are known to react oxidatively with simple olefins in the presence of Pd^{2+} salts. Carbon monoxide and hydrosilanes also take part in the telomerization. The telomerization reactions are surveyed based on the classification by the nucleophiles.

A. Reaction of Water

Formation of 2,7-octadienyl alcohol (**32**) by the reaction of water has attracted much attention as a novel practical synthetic method for *n*-octanol, which is of considerable industrial importance. However, the reaction of water under usual conditions of the butadiene telomerization is very sluggish. Atkins, Walker, and Manyik found that the presence of a considerable amount of carbon dioxide showed a very favorable effect on the telomerization of water (*40*). Reaction of water (2.0 moles) with butadiene (1.0 moles) using $\text{Pd}(\text{acac})_2$ and PPh_3 as the catalyst was carried out in the presence of carbon dioxide (0.5 mole) at 80–90°C. *tert*-Butyl alcohol, acetone, and acetonitrile were used as solvents. The products that were obtained are shown in Eq. (21) and Table I.



In the absence of carbon dioxide, only 1,3,7-octatriene (**16**) was formed. The effect of carbon dioxide is not clear. One explanation is via the

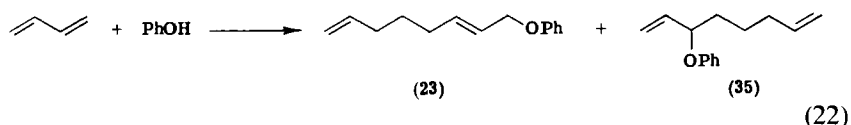
TABLE I

Solvents	Temp.	32 (%)	33 (%)	16 (%)	34 (%)
<i>tert</i> -Butyl alcohol	85°C	65	19	4	4
Acetone	90°C	69	7	13	10
Acetonitrile	82°C	56	4	6	6

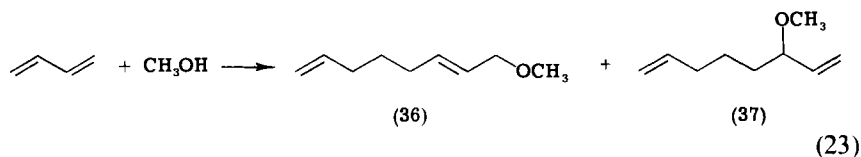
formation of octadienyl carbonate by the reaction of butadiene with carbonic acid followed by hydrolysis. Acidity of the medium seems to be important, and the telomerization of water proceeded in a solution buffered by mono- and disodium phosphate (41).

B. Reactions of Alcohols and Phenols

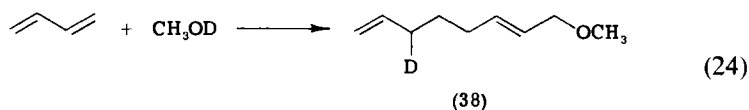
Phenol reacts with butadiene very smoothly to give octadienyl phenyl ether (23) in high yields. A branched ether (35) is a minor product.



Primary alcohols react easily to form ethers. Reaction of methanol was carried out at 70°C using $\text{Pd}(\text{PPh}_3)_2$ (maleic anhydride) as a catalyst to give 8-methoxy-1,6-octadiene (36) (85%) accompanied by 3-methoxy-1,7-octadiene (37) (5%) and 1,3,7-octatriene (3%) (42).

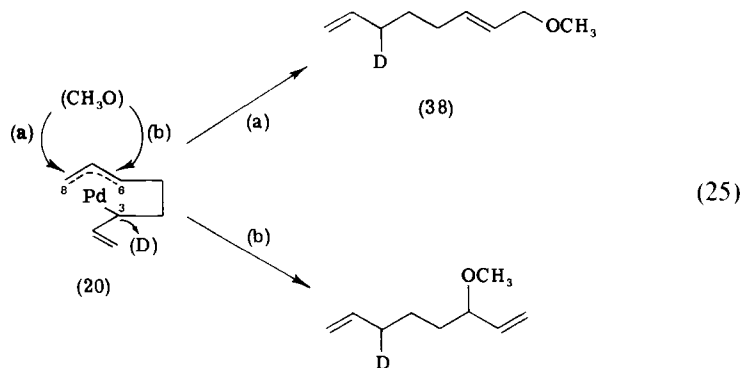


The dimerization reaction carried out in CH_3OD produced 8-methoxy-3-deuterio-1,6-octadiene (38) as a main product.

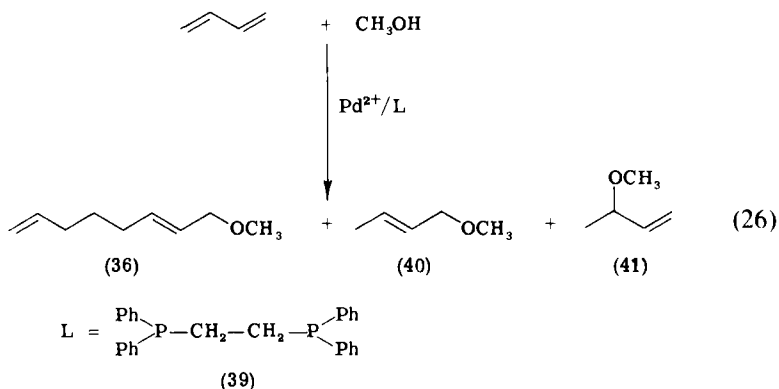


This result suggests the formation of the π -allyl complex (20) as an

intermediate. The telomers are formed by the 3,8- and 3,6-additions of (D) and (CH₃O) to the intermediate complex **20**:



Commereuc and Chauvin studied the effect of ligands on the reaction of ethanol (**43**). When bis(diphenylphosphino)-1,2-ethane (**39**) was used with PdCl₂ and sodium phenoxide, 1:1 products [1-methoxy-2-butene (**40**) and 3-methoxy-1-butene (**41**)] and a 1:2 product [8-methoxy-1,6-octadiene (**36**)] were obtained in equal amounts. Nickel-PEt₃ catalyst gave a mixture of the 1:2 and 1:1 telomers:

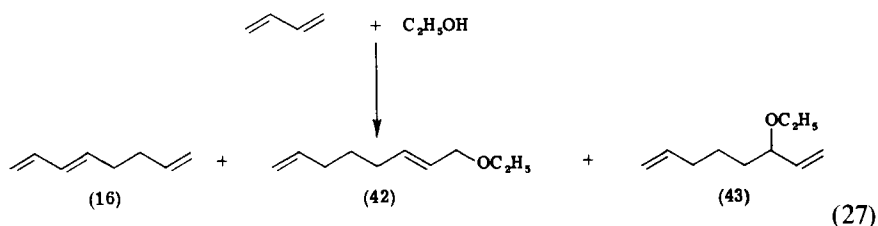


Green used the cationic phosphine palladium hydride complex for the reaction of methanol (**44**).

The reaction of ethanol carried out with Pd(PPh₃)₂ (maleic anhydride) produced 1,3,7-octatriene in 50% yield and 8-ethoxy-1,6-octadiene (**42**) in 33% yield (**31**). Beger and Reichel studied the effect of phosphine on this reaction and found that PBu₃, PPh₃, and P(Me₃N)₃ were satisfactory. PBu₃ gave the highest yield of the ether, as shown in Table II (**45**).

TABLE II

Phosphine	Conversion (%)	Ratio (%)		
		16	42	43
PBu ₃	100	8	89	3
PPh ₃	100	24	69	7
P(Me ₃ N) ₃	100	49	50	1
AsPh ₃	75	14	84	2
P(BuO) ₃	12	71	29	—



Telomerization of various primary and secondary alcohols has been carried out (45). The results obtained by using Pd(acac)₂ and PPh₃ at 60°C for 6 hours are shown in Table III. It can be said that primary alcohols react most easily with butadiene, but the higher the alcohol, the lower the reactivity to give the telomers. The reactivity of the secondary al-

TABLE III

ROH	Conversion (%)	Ratio (%)		
		16	8-Alkoxy-1,6-octadiene	3-Alkoxy-1,7-octadiene
CH ₃ OH	100	12	78	10
C ₂ H ₅ OH	100	24	69	7
<i>n</i> -C ₃ H ₇ OH	100	35	58	7
<i>i</i> -C ₃ H ₇ OH	100	29	64	7
<i>n</i> -C ₄ H ₉ OH	100	36	58	6
<i>i</i> -C ₄ H ₉ OH	100	46	52	2
<i>s</i> -C ₄ H ₉ OH	71	90	10	—
<i>t</i> -C ₄ H ₉ OH	69	67	—	—
<i>n</i> -C ₇ H ₁₅ OH	85	68	32	—
<i>n</i> -C ₁₀ H ₂₁ OH	67	71	29	—
<i>n</i> -C ₁₂ H ₂₃ OH	25	96	4	—
Cyclohexanol	31	49	—	—

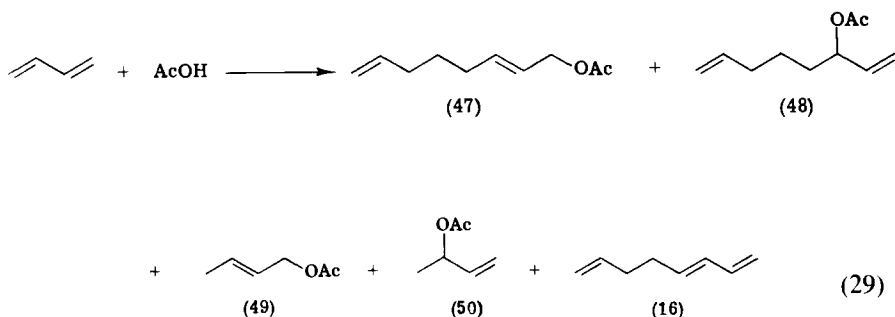
ardous. For example, Thiessen *et al.* (1961) presented data which were intended to bear on the way in which strychnine sulfate enhanced maze learning by rats, as reported by McGaugh and Petrinovich (1959). The dosage used in the Thiessen *et al.* study (1 mg/kg) was chosen because it was the same dosage used by McGaugh and Petrinovich. However, the former study was done on mice and the latter on rats. In one strain of mice, at least, the LD₅₀ for strychnine is less than one-half of that for one strain of rats (Longo *et al.*, 1959). Yet the results are taken by Thiessen *et al.* to cast doubt on the interpretation of McGaugh and Petrinovich, because the mice received injections of the drug "... in amounts previously shown to improve learning" (Thiessen *et al.*, 1961, p. 494). (For a complete discussion of this study, see McGaugh and Petrinovich, 1963a.)

Less widely recognized, however, are the less obvious, but equally important differences which exist between strains of the same species. Great differences in the results of behavioral manipulations are known to exist among representatives of the same species (Fuller and Thompson, 1960; Rosenzweig *et al.*, 1960). This point is often ignored, and, as a result, comparison of different studies and evaluation of the evidence on which different experimental conclusions are based are quite difficult.

B. PROBLEMS OF BEHAVIORAL TAXONOMY

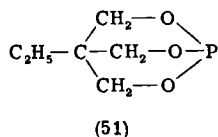
1. *Side Effects*

Any investigator who has studied the effects of drugs on any aspect of behavior is aware that side effects of drugs must be considered carefully in interpreting results. We have already mentioned Carlton's (1963) use of pairs of drugs of which one member is primarily central-acting and the other mainly peripheral-acting. If such pairs are not to be found within some families of drugs, one must rely on behavioral assessment of the drug's effects on those aspects of behavior known to be related to learning effectiveness. In some instances, drugs may enhance the performance of responses rather than affect the storage mechanism. For example, this might occur as a result of a change in hunger motivation or in emotionality. Therefore, measurements of hunger, emotionality, sensory thresholds, etc., are sometimes undertaken. This provides some information and hence a certain degree of control, but,



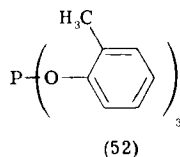
The reaction has been improved to a satisfactory process by modifying the reaction conditions. A remarkable effect of the addition of amines on the reaction was observed (49). For example, the reaction of butadiene (4 moles) and acetic acid (4 moles) in the presence of 2-(*N,N*-dimethylamino)ethanol (4 moles) using $\text{Pd}(\text{acac})_2$ (3 mmoles) and PPh_3 (3 mmoles) at 90°C gave complete conversion after 2 hours. The product was found to consist of 8-acetoxy-1,6-octadiene (47) (71%), 3-acetoxy-1,7-octadiene (48) (21%) and 1,3,7-octatriene (16) (8%). Various tertiary amines, such as triethylamine, *N*-methylmorpholine, *N,N,N',N'*-tetramethyl-1,3-butanediamine, and triethylenediamine, showed the same favorable effect. Other basic salts, such as sodium and potassium acetate, accelerate the reaction, especially at high concentrations (50, 51). The selection of solvents is also important. Arakawa and Miyake found that electron-donating type solvents (e.g., THF and triethylamine) are good solvents (50).

The effect of ligands has been studied (49). Phosphites, instead of phosphine, affect the ratio of isomers 47 and 48. Using triphenyl phosphite in the reaction of acetic acid at 50°C in 0.5 hour, 75% conversion of butadiene was attained. The selectivity to the acetoxyoctadienes was 93%, and the ratio of 47 to 48 was 92:8. Trimethylolpropanephosphite (51) completely eliminated the formation of 1,3,7-octatriene, and acetoxyoctadienes made up of 47 (81%) and 48 (9%) were obtained in the presence of *N,N,N',N'*-tetramethyl-1,3-butanediamine at 50°C in 2 hours' reactions.



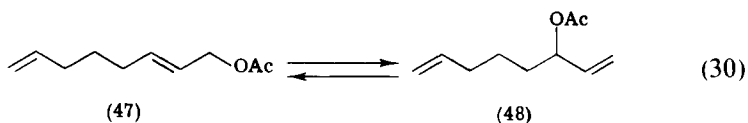
Rose and Lepper found that phosphites, especially *o*-substituted phenyl phosphites, enhance the catalytic activity of $\text{Pd}(\text{acac})_2$ or $\text{Pd}(\text{OAc})_2$ and affect the ratio of 47 to 48 (52). When $\text{Pd}(\text{OAc})_2$ and PPh_3 (1:1) were used at 50°C for 1.5 hours, the yield was 20% and the ratio of 47 to 48 was

1.2:1. In a similar reaction using tris(*o*-methylphenyl)phosphite (**52**), the yield was 97% and the ratio was 12.7:1. Furthermore, when the reaction was carried out at 25°C, the yield was 88% and the ratio was 28:1.



These results show that the *o*-substituted phosphites not only enhance the catalytic activity, but increase the selectivity of **47**.

The allylic acetate **47** can be isomerized to **48** by the palladium catalyst. When Pd(acac)₂ and PPh₃ were used, **47** was converted at 90°C for 12 hours into a 3.9:1 mixture of **47** and **48**. But the ratio remained 17:1 when tris(*o*-methylphenyl)phosphite (**52**) was used.



PdCl₂ and Pd(OAc)₂ anchored on a diphenylphosphinated polymer of styrene–divinylbenzene were used as the catalyst for the reaction of acetic acid. The product distribution was essentially the same for the reactions catalyzed by both homogeneous and anchored palladium catalysts (**53**).

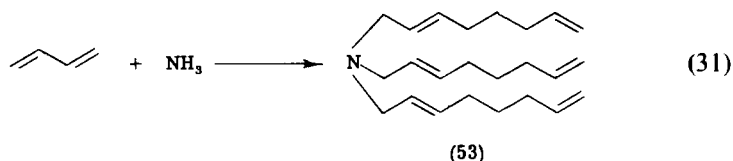
Few studies have been carried out on the telomerization of carboxylic acids other than acetic acid. Carboxylic acids are expected to react similarly with butadiene. The exception is formic acid: No telomerization takes place, as described before (**33**, **34**), and it behaves as a reductant rather than a nucleophile, forming 1,6- and 1,7-octadienes and octatriene.

1,3,7-Octatriene reacts further with butadiene in acetic acid by using π -allylic palladium complex as catalyst to give a mixture of acyloxydecatrienes (**54**).

D. Reactions of Ammonia and Amines

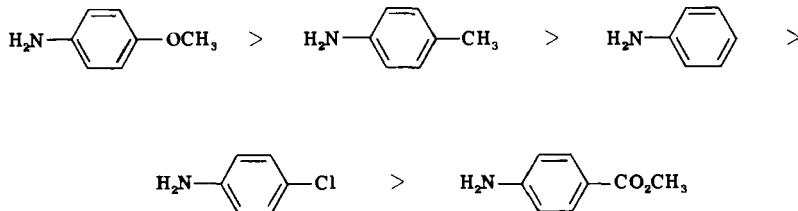
Direct addition of ammonia to olefinic bonds would be an attractive method of amine synthesis if it could be carried out smoothly, but so far facile addition of ammonia to simple olefins has not been reported. Like water, ammonia reacts with butadiene only under proper reaction conditions. A reaction of aqueous ammonia (28%, 5 g) with butadiene (32 g) in acetonitrile (60 ml) in the presence of Pd(OAc)₂ (63 mg) and PPh₃ (261

mg) at 80°C for 10 hours gave tri-2,7-octadienylamine (**53**) (29 g) as a main product, accompanied by a small amount of di-2,7-octadienylamine (1.2 g) (**55**). Also, isomeric branched triamines were formed as by-products. The reaction seems to proceed stepwise, but the primary amine is more reactive than ammonia, and the secondary amine is more reactive than primary amine. Thus, the main product was the triamine even when the reaction was stopped before completion.

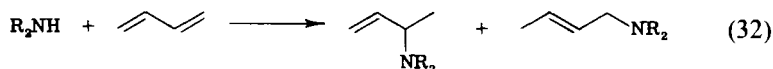


The reaction should be carried out in proper solvents which dissolve both butadiene and ammonia. Acetonitrile, dimethylformamide and *tert*-butyl alcohol are suitable solvents. Water seems to have a favorable effect on the reaction, and aqueous ammonia is superior to pure ammonia.

Reaction of amines with butadiene has been studied (31). Both aromatic and aliphatic amines react with butadiene to give tertiary amines. The following order of the reactivity with butadiene was observed with aniline derivatives.



A weak base such as carbazole gave a low conversion to amine adduct. No reaction took place with 2-pyrrolidone and acetamide. When bis(diphenylphosphino)ethane (**39**) was used as the ligand, 1:1 adducts were formed (56).

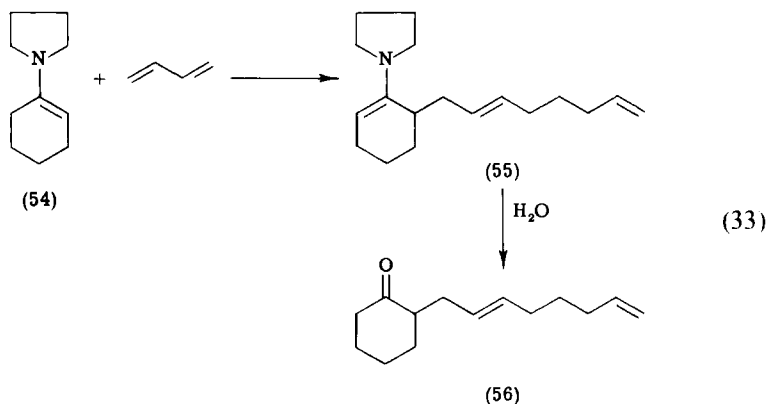


Amines with higher basicity showed higher reactivity. For example, the yields of the 1:1 adducts of morpholine ($\text{p}K = 9.61$), aniline (9.42), *n*-butylamine (3.39), and piperidine (2.80) were 79, 67, 19, and 29%, respectively. Telomerization of butadiene with diethylamine catalyzed by

bis- π -allyl complexes of nickel, palladium, and platinum afforded $\text{Et}_2\text{N}-(\text{C}_4\text{H}_6)_n-\text{H}$ ($n = 3$ and 4) (57).

E. Reactions of Enamines

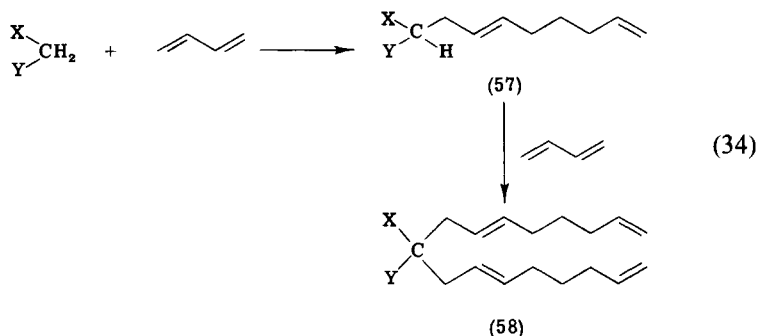
Enamines as nucleophiles react with butadiene, and the octadienyl group is introduced (58). In other words, enamines can be alkylated with butadiene. Because alkylated enamines are hydrolyzed easily to regenerate ketones or aldehydes, this is a good way to introduce the octadienyl group at the α position of ketones or aldehydes which do not react directly with butadiene. Pyrrolidine enamine of cyclohexanone (54) was allowed to react with butadiene using $\text{Pd}(\text{OAc})_2$ and PPh_3 at 80°C for 3 hours, and the product was hydrolyzed with dilute acid. As a main product, 2-(2,7-octadienyl)cyclohexanone (56) was obtained in high yield, accompanied by a small amount of 2,6-di(2,7-octadienyl)cyclohexanone. Pyrrolidine enamine of cyclopentanone behaved similarly to give mono- and dialkylated products in high yields.



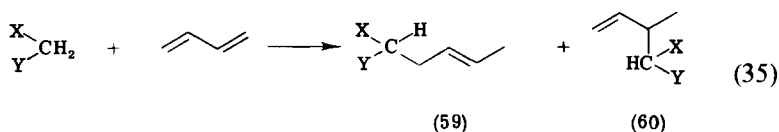
F. Reactions of Active Methylene and Methyne Compounds

Compounds with methylene and methyne groups to which are attached two electronegative groups, such as carbonyl, alkoxy carbonyl, formyl, cyano, nitro, and sulfonyl groups, react with butadiene smoothly; their acidic hydrogens are replaced with the 2,7-octadienyl group to give mono- and disubstituted compounds (59, 60). In addition, branched products are

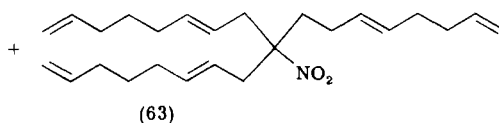
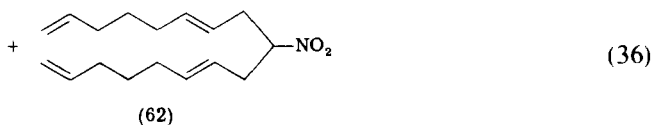
formed as by-products. The reactions of active methylene compounds give two kinds of main products, the 1:2 adduct (**57**) and the 1:4 adduct (**58**). At an earlier stage of the reaction, the product consisted mainly of the 1:2 adduct. Further addition of butadiene affords the 1:4 adduct:



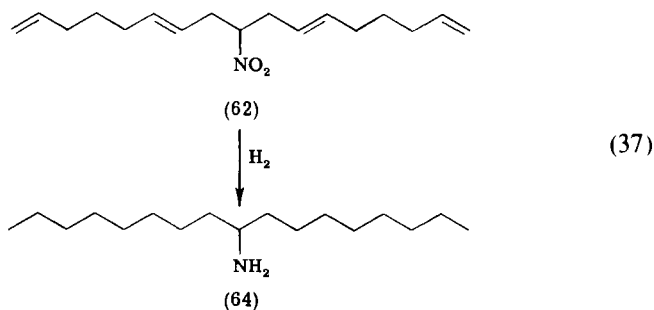
The reaction was carried out with β -keto esters, β -diketones, malonate, α -formyl ketones, α -cyano and α -nitro esters, cyanoacetamide, and phenylsulfonylacetate. $(\text{PPh}_3)_2\text{PdCl}_2$ was used with sodium phenoxide. Also, $\text{Pd}(\text{OAc})_2$ and PPh_3 are good catalysts. When bidentate ligand was used, the 1:1 rather than 1:2 addition reaction took place (**56**). For example, bis(diphenylphosphino)1,2-ethane (**39**) produced a mixture of the following 1,4- (**59**) and 1,2- (**60**) addition products:



In general, methylene and methyne groups activated by one electron-donating group are not active for the telomerization. Simple ketones and esters, for example, are inert. Actually, acetone and ethyl acetate are used as good solvents for the telomerization. One exception is nitroalkanes, which react with butadiene smoothly; their α -hydrogens are replaced with 2,7-octadienyl groups to give long-chain nitroalkenes (**55**, **61**). When there are two or three α -hydrogens, the octadienyl group is introduced successively. It is possible to stop the reaction at a certain stage by adjust the relative amounts of the reactants and reaction time. From nitromethane, the products **61**–**63** were formed, accompanied by 3-substituted 1,7-octadiene as a minor product:



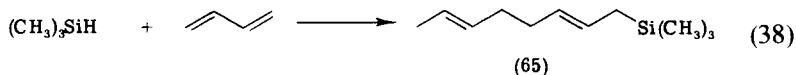
In this telomerization, selection of proper conditions is essential for achieving high yield of the nitroalkenes. Otherwise, simple oligomerization of butadiene predominates as a competing reaction. Solvents have a large influence on the reaction, and *tert*-butyl alcohol was found to be a good solvent. $\text{Pd}(\text{OAc})_2$ or $\text{Pd}(\text{acac})_2$ is used with PPh_3 . Also, $\text{PdCl}_2(\text{PPh}_3)_2$ is used with KOH or sodium phenoxide. These bases also showed an accelerating effect: The reaction proceeded faster and gave higher yields when the ratio of KOH to $\text{PdCl}_2(\text{PPh}_3)_2$ was above 100. One mole of palladium catalyst easily produced more than 1000 moles of the nitroalkenes. The reaction proceeded even at room temperature. A higher temperature accelerated the reaction but at the same time increased the amount of 1,3,7-octatriene. The nitro compounds synthesized by this reaction are hydrogenated to give saturated long-chain amines (**64**) which have a primary amino group at the middle of the carbon chain. These



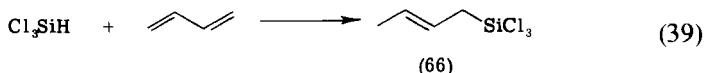
amines are expected to have properties different from common long-chain amines which have amino groups at the terminal position.

G. Reactions of Silicon Compounds

Hydrosilanes react with butadiene by the catalysis of palladium compounds, but the nature of the reaction is somewhat different from that of the telomerization of other nucleophiles described before. Different products are obtained depending on both the structure of silanes and the reaction conditions. Trimethylsilane and other trialkylsilanes reacted with butadiene to give the 1:2 adduct, 1-trialkylsilyl-2,6-octadienes (**65**), in high yield (98%) (62–64). Unlike other telomers which have the 1,6-octadienyl chain, the telomers of silanes have the 2,6-octadienyl chain. As catalysts, $\text{Pd}(\text{PPh}_3)_2$ (maleic anhydride), $\text{PdCl}_2(\text{PhCN})_2$, PdCl_2 , and π -allylpalladium chloride were used. Methyl-diethoxysilane behaved similarly to give the 1:2 adduct.



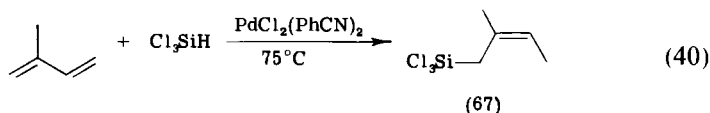
However, in addition to the 1:2 adduct, the 1:1 adduct was also formed, depending on the structure of silanes (64–66). Thus, trichlorosilane reacted to give 1-trichlorosilyl-2-butene (**66**) as the 1:1 adduct selectively in 93.5% yield at 100°C. Trichlorosilane is more reactive than trialkylsilanes.



A mixture of 1:1 and 1:2 adducts (83.5 and 5.2%) was obtained with dichloromethylsilane (65).

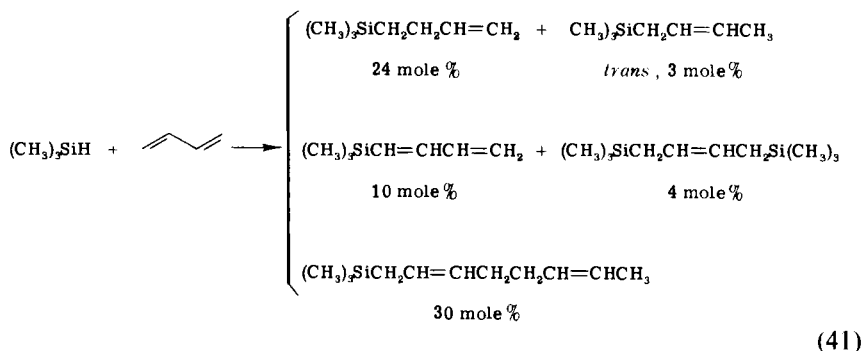
The hydrosilylation of butadiene proceeds with palladium compounds even in the absence of phosphines. Other ligands, such as glyoxime, benzonitrile, and 1,5-cyclooctadiene, can be used as effective ligands for the hydrosilylation of butadiene (65, 67). The reaction of trichlorosilane and dichlorosilane with isoprene proceeded regioselectively and stereoselectively to give *Z*-1-trichlorosilyl-2-methyl-2-butene (**67**) (65, 66, 68). No reaction of trimethylsilane with isoprene took place, and this shows the lower reactivity of trialkylsilane.

It appeared at first that the differentiation in the formation of the 1:1 and 1:2 adducts was solely dependent on the structure of silanes as



described above. However, further studies carried out by Hetflejs and co-workers revealed that the formation of the 1:1 and 1:2 adducts is dependent on structures of silanes, on reaction conditions, and on palladium catalysts. A considerable amount of the 1:1 adduct was obtained by the reaction of alkyl or alkoxy silanes. For example, the ratio of the 1:1 and 1:2 adducts in the reaction of triethoxysilane changed by the reaction conditions as shown in Table IV (69).

The reaction of trimethylsilane was found to be less selective at elevated temperatures. The following products were formed using $\text{PdCl}_2(\text{PhCN})_2$ in benzene at 100°C (70):

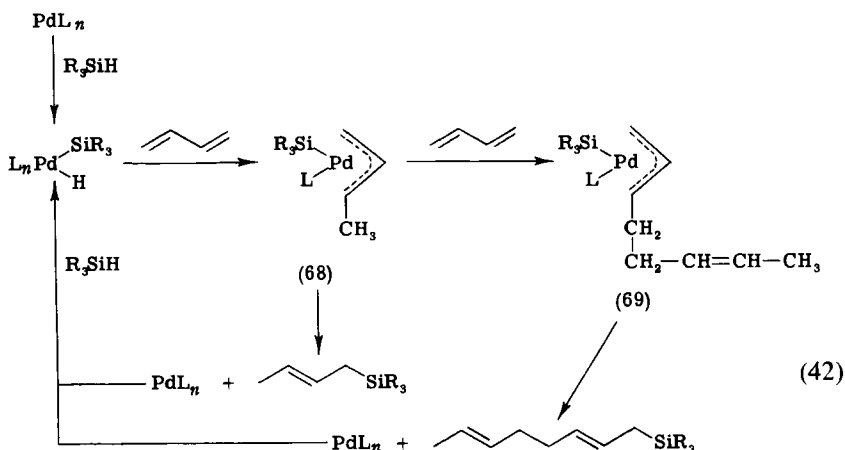


It can thus be concluded that the formation of the 1:1 adduct is favored by higher temperature and the absence of stabilizing ligands such as phosphine, although the structure of the silanes seems to be the most important factor.

TABLE IV
REACTIONS OF BUTADIENE WITH TRIETHOXYSIANE

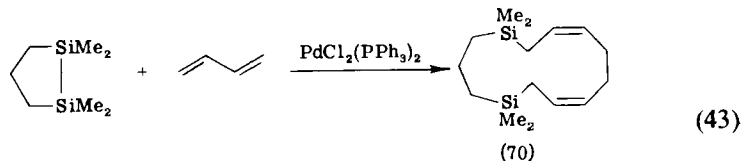
Catalyst	Reaction temp. (°C)	Yield (%)		Overall yield (%)
		1:1	1:2	
$\text{PdCl}_2(\text{PhCN})_2$	22	9	91	100
	100	15	51	66
$\text{PdCl}(\pi\text{-C}_3\text{H}_5)$	22	8	92	100
	100	45	20	65
$\text{PdCl}_2(\text{PPh}_3)_2$	100	35	38	73

In order to explain the competitive formation of the 1:1 and 1:2 adducts and the formation of the 2,6-octadienyl rather than the 1,6-octadienyl chain, a mechanism was proposed (62, 69) in which the insertion of one mole of butadiene to the Pd—H bond gives the π -methallyl complex (68) at first, from which 1-silylated 2-butene is formed. At moderate temperature and in the presence of a stabilizing ligand, further insertion of another molecule of butadiene takes place to give C₅-substituted π -allyl complex 69. The reductive elimination of this complex gives the 1:2 adduct having 2,6-octadienyl chain. In the usual telomerization of the nucleophiles, the reaction of butadiene is not stepwise and the bis- π -allylic complex 20 is formed, from which the 1,6-octadienyl chain is liberated.

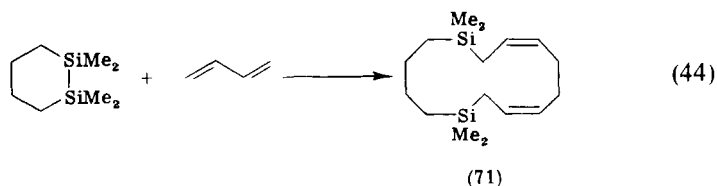


Hydrosilylation of butadiene using palladium complexes supported on inorganic materials such as silica and alumina has been carried out (71, 72); however, the supported catalyst is not stable and it is difficult to compare with the soluble catalysts.

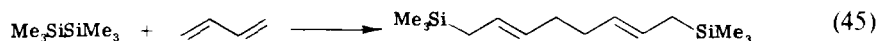
Cyclic carbodisilanes undergo addition reactions with conjugated dienes with splitting of their Si—Si bond. 1,1,2,2-Tetramethyl-1,2-disilacyclopentane reacted with butadiene by the catalysis of $\text{PdCl}_2(\text{PPh}_3)_2$ at 100°C to give 1,1,5,5-tetramethyl-1,5-disilacyclotrideca-7,11-diene (70) in



83% yield (73). Similar reaction with isoprene gave 1,1,5,5,8,11-hexamethyl-1,5-disilacyclotrideca-7,11-diene in 76% yield. Six-membered carbodisilanes underwent similar reactions to give the 14-membered compound 71.

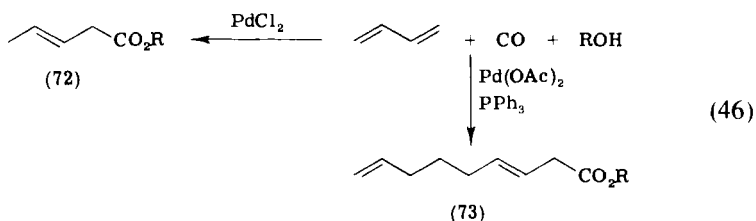


Unstrained organodisilanes reacted slowly with splitting of the Si—Si bond:



H. Carbonylation Reactions

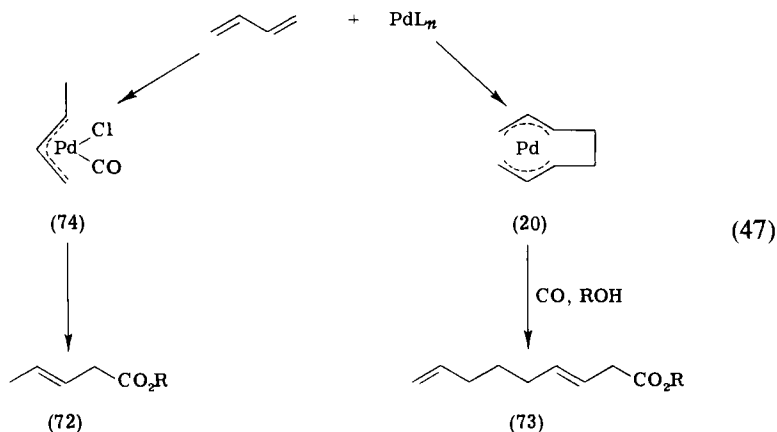
Simple carbonylation and dimerization-carbonylation of butadiene take place in alcohol depending on the catalytic species of palladium. When PdCl_2 is used as a catalyst with or without PPh_3 , 3-pentenoate (72) is the sole product (74, 75). On the other hand, when $\text{Pd}(\text{OAc})_2$ is used with PPh_3 , the dimerization-carbonylation takes place to give 3,8-nona-dienoate (73) (76, 77).



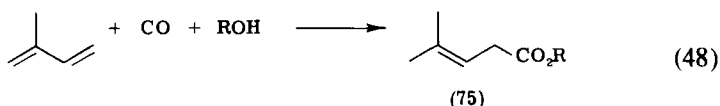
The essential factor which differentiates the monomeric and dimeric carbonylations seems to be the presence or absence of halide ion coordinated to the palladium. The dimerization-carbonylation proceeds satisfactorily with halide-free palladium phosphine complexes. Most conveniently, $\text{Pd}(\text{OAc})_2$ is used with PPh_3 . $\text{PdCl}_2(\text{PPh}_3)_2$ can be used as a catalyst with addition of an excess of bases. The reaction is carried out at 110°C under 50 atm of carbon monoxide pressure in alcohol. Higher

carbon monoxide pressure tends to decrease the yield of the esters. Any alcohol can be used except methanol, in which almost no reaction takes place. In order to prepare methyl nonadienoate, the reaction should be carried out in a suitable solvent, e.g., acetonitrile-containing methanol. Even in *tert*-butyl alcohol, the carbonylation proceeds smoothly to give *tert*-butyl ester in high yield.

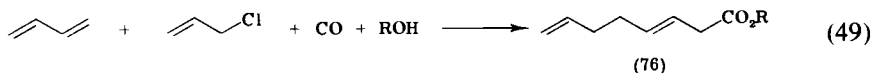
The carbonylation was explained by the following mechanism. Formation of dimeric π -allylic complex **20** from two moles of butadiene and the halide-free palladium species is followed by carbon monoxide insertion at the allylic position to give an acyl palladium complex which then collapses to give 3,8-nonadienoate by the attack of alcohol with regeneration of the zero-valent palladium phosphine complex. When halide ion is coordinated to palladium, the formation of the above dimeric π -allylic complex **20** is not possible, and only monomeric π -allylic complex **74** is formed. Carbon monoxide insertion then gives 3-pentenoate (**72**).



No dimerization-carbonylation takes place with isoprene, irrespective of the catalytic species (**78**). Selective formation of 4-methyl-3-pentenoate (**75**) was observed in alcohol by the catalysis of either PdCl_2 or $\text{Pd}(\text{OAc})_2$ and PPh_3 :

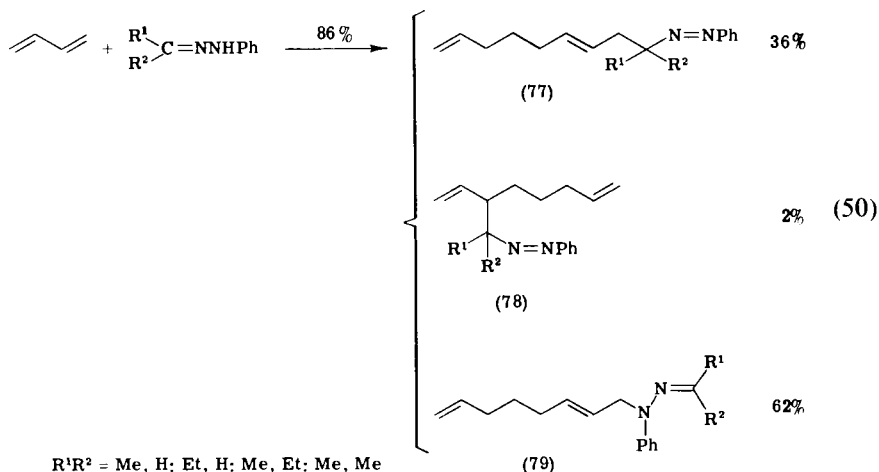


Carbonylation of a mixture of allyl chloride and butadiene with PdCl_2 was carried out, and 3,7-octadienoate (**76**) was obtained as one product (**79**, **80**):



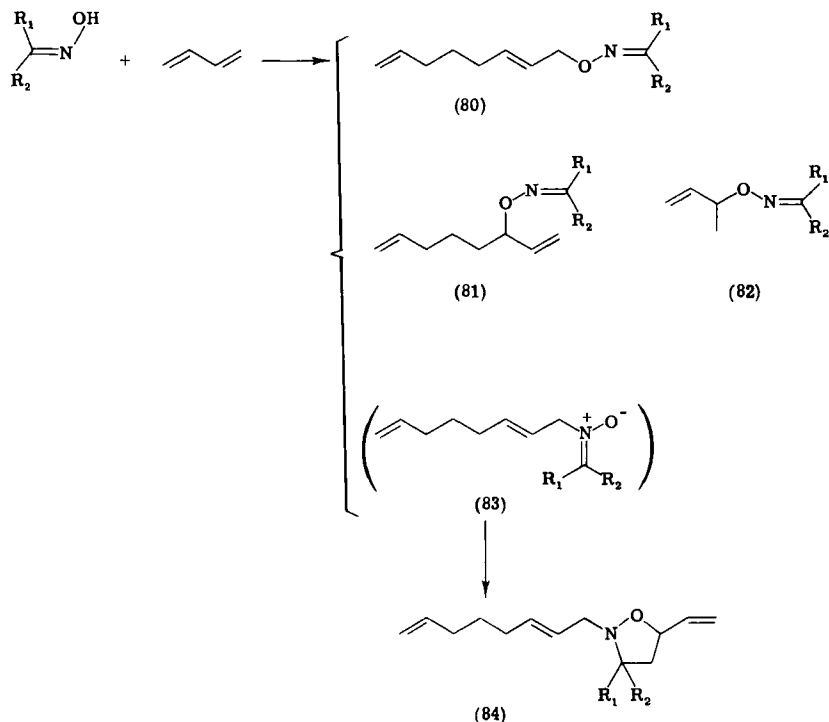
I. Reactions of Phenylhydrazones and Oximes

The reaction of phenylhydrazones with butadiene was carried out by Baker on the basis of the idea that phenylhydrazones have both nucleophilic nitrogen and electrophilic carbon. Products **77**–**79** were obtained by the reaction of phenylhydrazones with $\text{Pd}(\text{PPh}_3)_4$ (81):



Two azo products (**77**, **78**) were suggested to arise from the reaction of the π -allyl group at the electrophilic carbon atom followed by hydrogen shift. Also, a product from octadienylation of nitrogen of the hydrazone was formed (**79**). In contrast, reaction of *N*-methylhydrazones with butadiene gave only the latter product in the presence of palladium catalysts (82). Although the ratio of the products was different, the same products were obtained by the reactions of hydrazones and imines using zero-valent nickel complex coordinated by PPh_3 (81, 83).

In the reaction of oximes with butadiene catalyzed by $\text{Pd}(\text{PPh}_3)_4$ or $\text{Pd}(\text{NO}_3)_2$ and PPh_3 , the octadienylation proceeded at either oxygen or nitrogen to yield oxime ethers **80** and **81** and nitrones **83**, the latter reacting thermally with butadiene to yield *N*-alkylated isoxazolidines **84** (84). In addition, butenyl ethers such as **82** were obtained. The ratio of these products changed depending on the structure of oximes. For example, aliphatic aldehyde oximes gave isoxazolidines (**84**) exclusively:



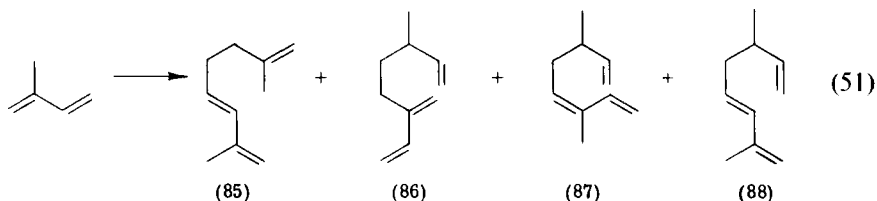
V

DIMERIZATION AND TELOMERIZATION OF ISOPRENE

Telomerization or dimerization of isoprene, if carried out regiospecifically to give a head-to-tail dimer or telomer, would be a very useful method for terpene synthesis. Active studies and synthetic attempts have been carried out aiming at the regiospecific dimerization and telomerization of isoprene using palladium catalysts. In general, the reaction of isoprene is slower than that of butadiene. In addition, a mixture of dimers and telomers is usually obtained. So far, a few reports of the palladium-catalyzed regiospecific dimerization of isoprene have been published. The distribution of isomeric dimers produced by palladium catalysis is dependent on the ligand and solvents employed and on the reaction temperature. Lower temperatures tend to afford higher selectivity.

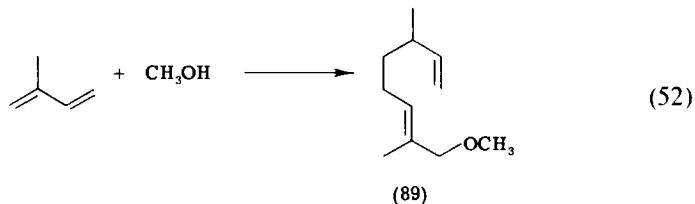
The dimerization of isoprene was carried out by a catalyst system of $\text{PdBr}_2/\text{bis}(\text{diphenylphosphino})-1,2\text{-ethane}$ (39) sodium phenoxide at 150°C for 1 hour in benzene (85). Catalytic activity was enhanced by the addition

of phenol. Furthermore, distribution of the isomers was remarkably affected by the molar ratio of phenol to isoprene. When the ratio (phenol:isoprene) was 1:30, the tail-to-tail dimer, 2,7-dimethyl-1-*trans*-3,7-octatriene (**85**), was formed almost selectively. On the other hand, the ratio of 1:1.5 leads to head-to-head dimerization to give 2-vinyl-5-methyl-1,6-heptadiene (**86**) and 3,6-dimethyl-1-*cis*-3,7-octatriene (**87**) as main products. With the 1:3 ratio of phenol to isoprene, the dimer consisted mainly of 2,6-dimethyl-1-*trans*-3,7-octatriene (**88**) derived from the head-to-tail dimerization. Probably in this reaction, phenoxy ethers are the primary products, and subsequent elimination of phenol took place to give isoprene dimers:

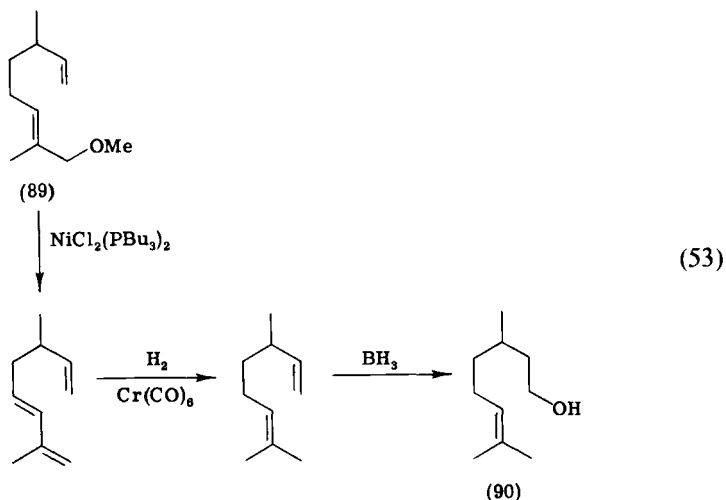


2,7-Dimethyl-1,3,7-octatriene (**85**) was obtained as a main product (70% yield, 90% selectivity) by using $\text{Pd}(\text{acac})_2/\text{PPh}_3$ at 65°C in the presence of *m*-methoxybenzaldehyde (**86**). In the absence of the aldehyde, yield of the dimer was 12% and selectivity was low. Josey reported that in acetone solution with $\text{Pd}(\text{PPh}_3)_2$ (maleic anhydride) at 105°C , isoprene gave mainly 2,7-dimethyl-1,3,7-octatriene (**85**) by the tail-to-tail addition (**87**). Musco obtained **85** as a main product at 110°C in the presence of carbon dioxide (**88**). In the absence of carbon dioxide, the conversion was low. PEt_3 and tricyclohexylphosphine were found to be better ligands than PPh_3 for the reaction of isoprene.

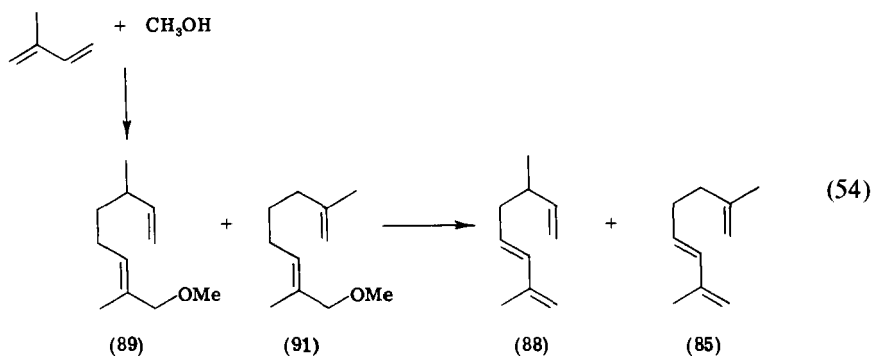
A successful selective head-to-tail telomerization to give 1-methoxy-2,6-dimethyl-2,7-octadiene (**89**) by the reaction of isoprene with methanol at room temperature was reported by Yamazaki (**89**). Although the reaction is the selective head-to-tail addition, unfortunately the methoxy group was introduced at the position opposite to oxygen function in natural products:



Hidai and Uchida reinvestigated this reaction. The product was converted to citronellol (**90**) by the following sequence of reactions (**90**):



Asymmetric telomerization of isoprene and methanol by using chiral phosphines, such as menthyldiphenylphosphine, gave an optical yield of 17.6%. The telomerization of methanol and isoprene using π -allylpalladium chloride and PBu_3 in the presence of sodium methoxide in a mixed solvent of methanol and isopropyl alcohol at room temperature for 2 days produced 1-methoxy-2,6-dimethyl-2,7-octadiene (**89**) (80%) and 1-methoxy-2,7-dimethyl-2,7-octadiene (**91**) (15%) (*91*). After 2 days, the reaction mixture was heated at 80°C for 8 hours, and 2,6-dimethyl-1,3,7-octatriene (**88**) (75%) and 2,7-dimethyl-1,3,7-octatriene (**85**) (14%) were obtained. Also, $\text{NiCl}_2(\text{Bu}_3\text{P})_2$ was used as a cocatalyst for the formation of **88**.

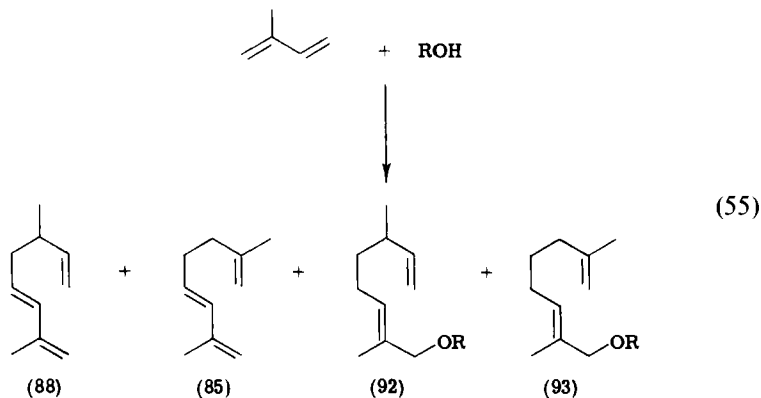


The regioselectivity observed in the telomerization of methanol is

TABLE V

Alcohols	Conversion (%)	Ratio (%)		
		Dimer 88 + 85	92	93
MeOH	100	43	30	27
EtOH	100	73	14	13
<i>n</i> -PrOH	55	88	6	6
<i>i</i> -PrOH	50	53	32	15
<i>n</i> -BuOH	48	88	5	7
<i>i</i> -BuOH	42	100		
<i>s</i> -BuOH	32	100		
<i>t</i> -BuOH	24	89		

highly dependent on reaction conditions, especially temperature. Extensive studies carried out by Beger and co-workers in methanol and other alcohols showed that the telomerization of isoprene is not selective (92). As shown in Table V, a mixture of the head-to-tail and tail-to-tail dimers and telomers was obtained in alcohols at 80°C for 10 hours by using Pd(acac)₂ and PPh₃ (1:2 molar ratio).



The results in Table VI were obtained by the reactions at 80°C with Pd(acac)₂ using different ligands in a mixture of methanol and isopropyl alcohol. From these results, it seems likely that reaction temperature has large influence on the regiospecificity of the telomerization. As another example, a mixture of isomeric telomers was obtained by the reaction of methanol and isoprene at 100° (93).

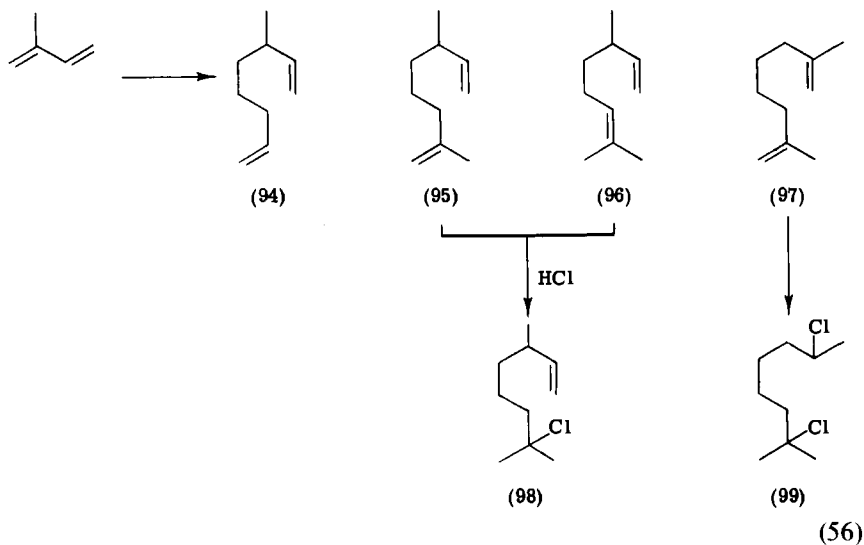
A mixture of isomeric monomeric and dimeric telomers was obtained

TABLE VI

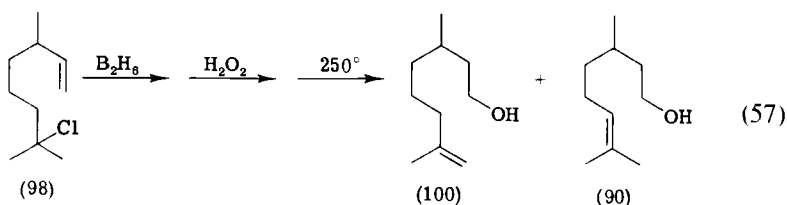
Ligands	Conversion (%)	Ratio (%)		
		Dimer 88 + 85	92	93
PPh ₃	100	40	33	27
<i>n</i> -Bu ₃ P	100	36	44	20
<i>i</i> -Bu ₃ P	100	36	40	24
(Me ₂ N) ₃ P	75	67	26	7
(<i>o</i> -PhPhO) ₃ P	70	66	21	13
Ph ₃ As	65	38	32	30
(PhO) ₃ P	17	66	21	13

by the reaction of acetic acid with isoprene catalyzed by PdCl₂/PPh₃ in the presence of sodium acetate (94).

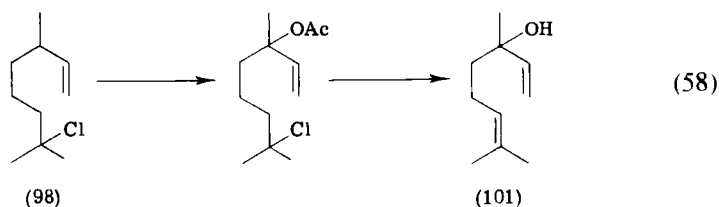
Heck tried the reductive dimerization of isoprene in formic acid in the presence of triethylamine at room temperature using 1% palladium phosphine catalysts to give dimers in up to 79% yield (95). Better selectivity to the head-to-tail dimer was obtained by using Pd(OAc)₂ with 1:1 ratio of arylphosphines. THF as solvent showed a favorable effect. In a scaled-up reaction with 0.5 mole of isoprene using π -allylpalladium acetate and *o*-tolylphosphine, the isolated yield of the dimers was 87%. The dimers contained 71% of the head-to-tail isomers. The mixture was converted into easily separable products by treatment with concentrated hydro-



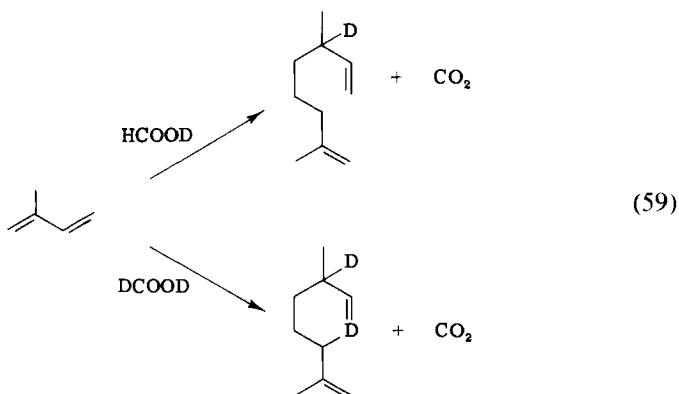
chloric acid at room temperature. Only di- and trisubstituted double bonds reacted with hydrochloric acid; terminal monosubstituted double bonds were unaffected. The head-to-head dimer **94** remained intact, and the tail-to-tail dimer **97** formed dichloride **99**. The desired head-to-tail dimers, **95** and **96**, gave the monochloride, namely, 7-chloro-3,7-dimethyl-1-octene (**98**) in 84% yield based on the head-to-tail dimers present. The monochloride was converted into α - and β -citronellols (**100**, **90**):



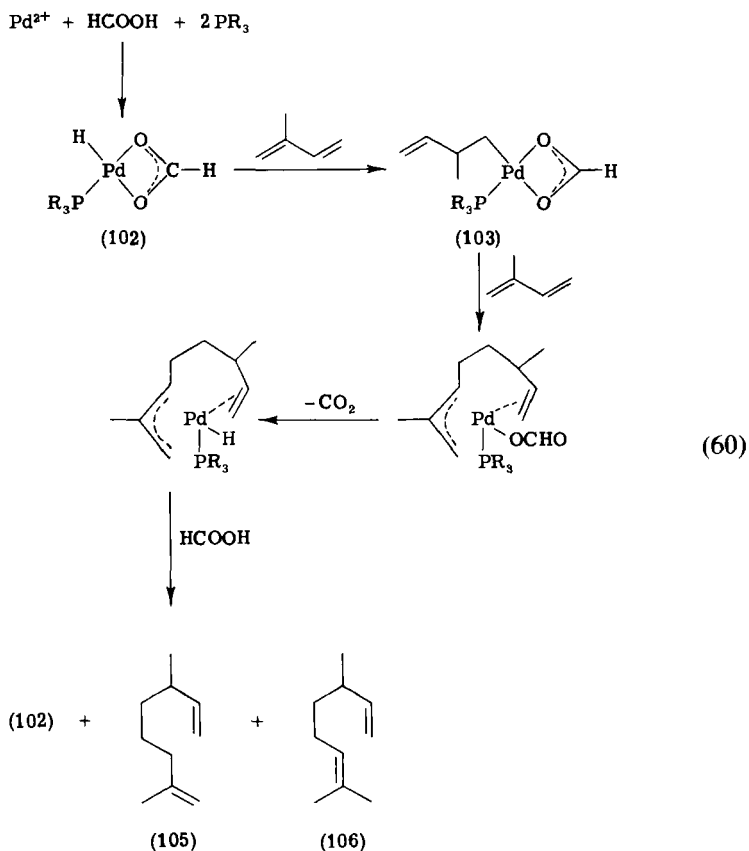
Linalool (**101**) was prepared as follows:



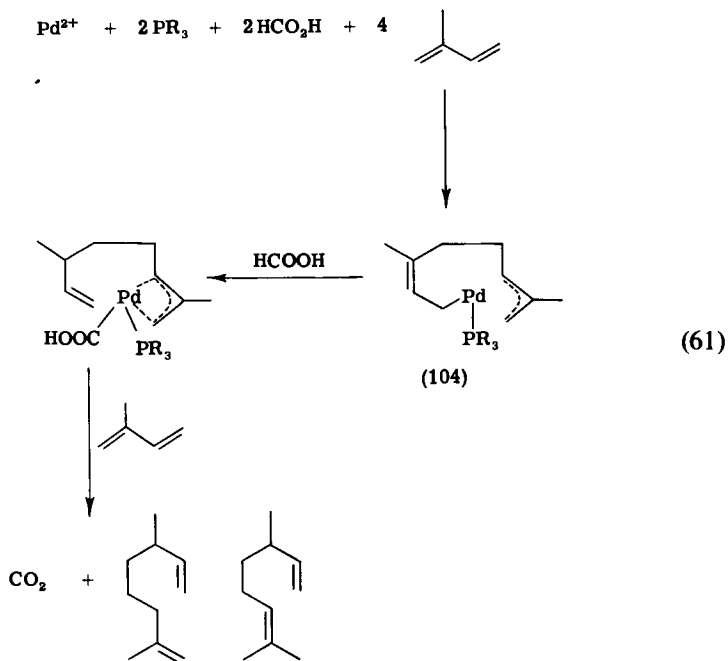
The mechanism of the reductive dimerization was studied by using both dideuterated and carboxyl-deuterated formic acid. The carboxyl deuterium was found on carbon 6, and the other deuterium on carbon 3 of 2,6-dimethyl-1,7-octadiene.



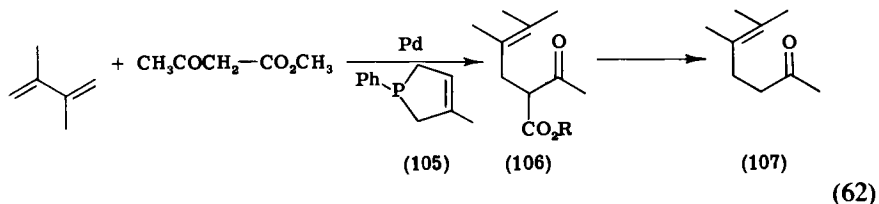
In one mechanism, Pd^0 generated by reduction of Pd^{2+} with formic acid forms hydridoformatopalladium complex **102**, which reacts with isoprene to form formato(methylbutenyl)palladium complex **103**. Then, insertion of the second molecule of isoprene takes place. Finally, reductive elimination and evolution of carbon dioxide give the dimers: (60)



In the second mechanism, coupling of two moles of isoprene on Pd^0 forms a dimethyloctadienediylpalladium complex (**104**) which is then reduced by formic acid with evolution of carbon dioxide:



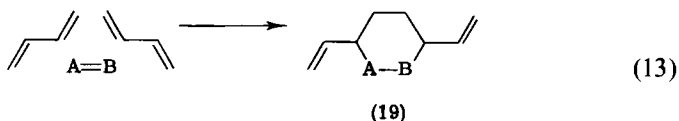
One mole of isoprene reacted with one mole of acetoacetate by using a bidentate phosphine as ligand (56). Reaction of 2,3-dimethylbutadiene with acetoacetate was carried out by using PdCl_2 in the presence of sodium phenoxide. When PPh_3 was used, a 1:2 adduct was obtained. On the other hand, use of P-phenyl-1-phospha-3-methyl-3-cyclopentene (**105**) at 100°C caused the 1:1 addition to give 3-carbomethoxy-5,6-dimethyl-5-hepten-2-one (**106**), from which 5,6-dimethyl-5-hepten-2-one (**107**) was formed. This compound is the useful intermediate for α -irone synthesis (96).



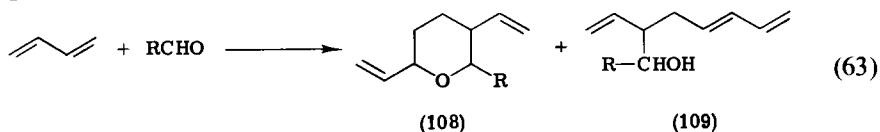
VI

CYCLIZATION REACTIONS

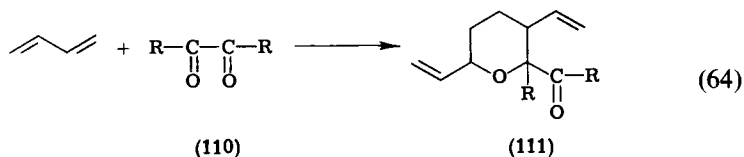
Unlike nickel catalysts, palladium complexes do not catalyze the homocyclization reaction to give CDT or COD. The difference seems to be due to a different degree of hydride shift and atomic volume. With palladium catalysts, the hydride shift is easier, and hence linear oligomers are formed. The characteristic reaction catalyzed by palladium is the cocyclization of two moles of butadiene with one-hetero atom double bonds such as C=N and C=O bonds to give six-membered rings with two vinyl groups (19):



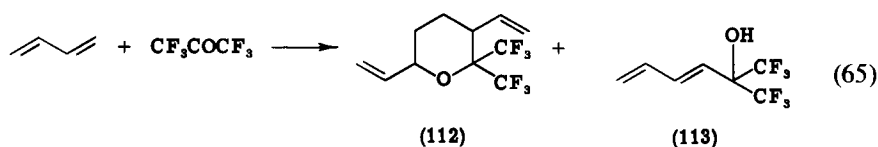
A typical reaction is the formation of 2-substituted 3,6-divinyltetrahydropyranes (108) by the reaction of butadiene with aldehydes (97–100). In this reaction, unsaturated noncyclized alcohols 109 are also formed. The selectivity to the pyranes and alcohols can be controlled by the ratio of Pd and PPh₃ in the catalyst system. When the ratio was higher than 3, pyranes were formed exclusively. On the other hand, with the lower ratio of Pd and PPh₃, the unsaturated alcohols were formed as the main product.



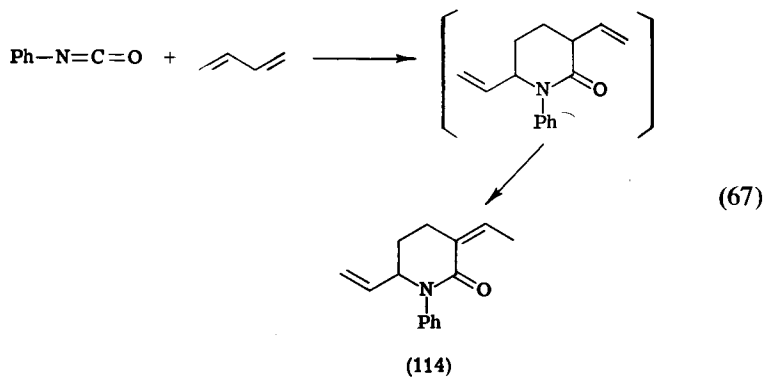
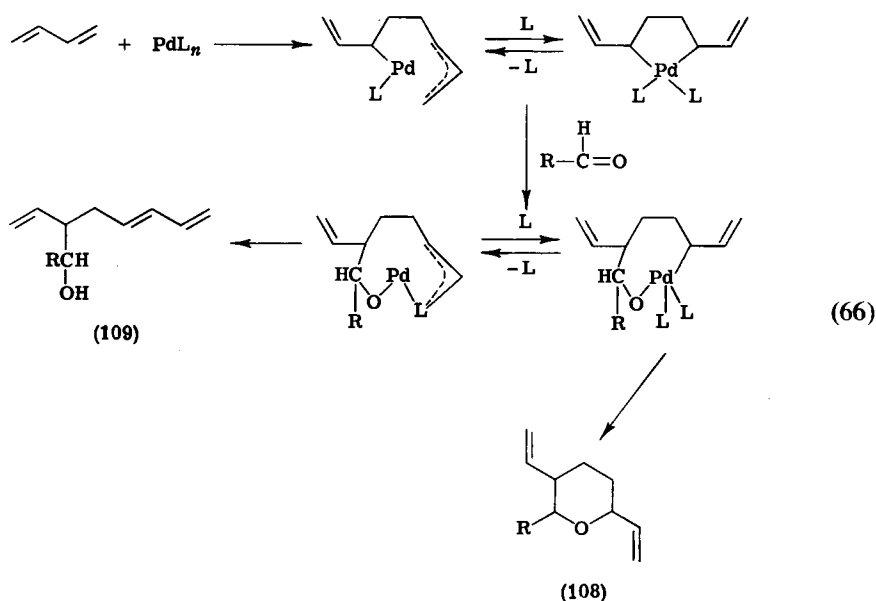
The reaction of benzaldehyde with butadiene at 80°C for 10 hours in the presence of a catalytic amount of Pd(OAc)₂ and PPh₃ gave 1-phenyl-2-vinyl-4,6-heptadien-1-ol (109, R = Ph) and 2-phenyl-3,6-divinyltetrahydropyran (108, R = Ph) in 90% yield. In this reaction, the carbonyl group of aldehydes reacts to give pyranes. Both aliphatic and aromatic aldehydes including formaldehyde behave similarly. However, carbonyl groups of ketones and ester do not react with butadiene. The exception is the α-diketones 110, which reacted with one of their carbonyl groups (98):



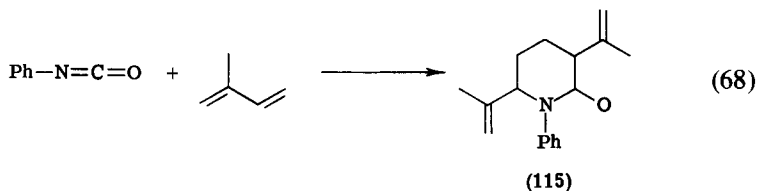
In addition, perfluoroacetone reacted with butadiene to give 2,2-bis(trifluoromethyl)-3,6-divinyltetrahydropyran (**112**) and 1,1,1-trifluoro-2-trifluoromethyl-3,5-hexadien-2-ol (**113**).



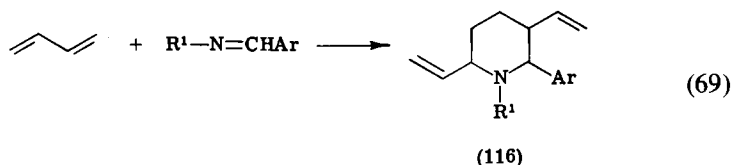
The formation of **108** and **109** was explained by the following mechanism [Eq. (66)] (98):



Another molecule which takes part in the cocyclization [see Eq. (67)] is arylisocyanate. The C=N double bond, rather than the C=O double bond in phenylisocyanate, reacts with butadiene to give 3-ethylidene-1-phenyl-6-vinyl-2-piperidone (**114**) in 75% yield. In this reaction, the double bond migration to the conjugated position took place (101). With isoprene, the selective head-to-head dimerization-cyclization took place at 100°C to give 3,6-diisopropenyl-1-phenyl-2-piperidone (**115**).



The C=N double bond in Schiff bases also reacted with butadiene to give 3,6-divinylpiperidones (**116**) (102). For this reaction, $\text{Pd}(\text{NO}_3)_2$ and $\text{PPh}_3(1:3)$ were used as a suitable catalyst:



Only the Schiff bases of aromatic aldehydes took part in the reaction. When $\text{R}^1 = \text{CH}_3$, the piperidone was obtained as a mixture of stereoisomers in 73% yield at 80°C for 10 hours.

With nickel complexes, these cocyclizations are not possible. A related reaction is the cocyclization of butadiene with azines to give 12-membered heterocyclic compounds **9** (11) [see Eq. (3)].

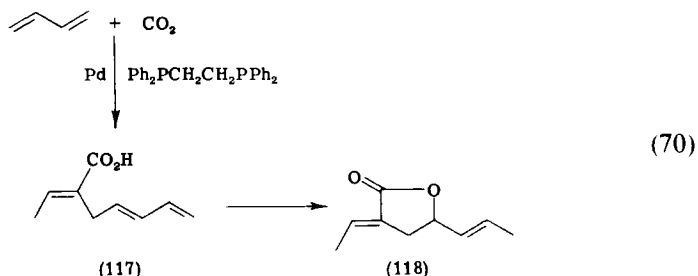
VII

REACTIONS OF CARBON DIOXIDE

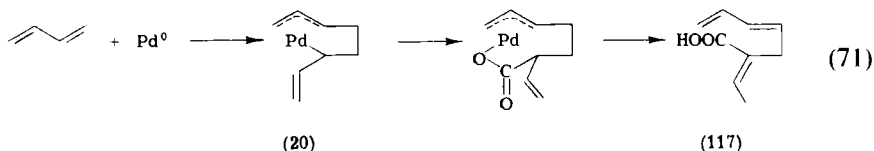
There appeared several reports treating the activating effect of carbon dioxide on the dimerization or telomerization of butadiene, as described before. But in none of these reactions did carbon dioxide behave as a reactant. Sasaki, Inoue, and Hashimoto found that carbon dioxide was incorporated to a small extent into the dimer of butadiene (103).

The reaction carried out at 120°C in DMF using a palladium catalyst coordinated by bis(diphenylphosphino)-1,2-ethane (**39**) produced 2-ethyl-

idene-4,6-heptadienoic acid (**117**) in 4–12% yield. When isolated, the acid lactonized very easily to form the lactone **118**.



The following mechanism was proposed for the reaction of carbon dioxide with butadiene:



VIII

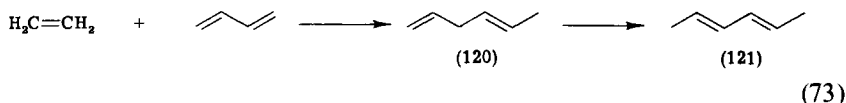
COOLIGOMERIZATION OF BUTADIENE WITH OLEFINS

Cooligomerization of butadiene with some olefinic compounds has been carried out. Two moles of allene reacted at 120°C with butadiene by the catalysis of $\text{Pd}(\text{PPh}_3)_2$ (maleic anhydride) to give *cis*- and *trans*-2-methyl-3-methylene-1,5,7-octatriene (**119**) in 39% yield (*104*):

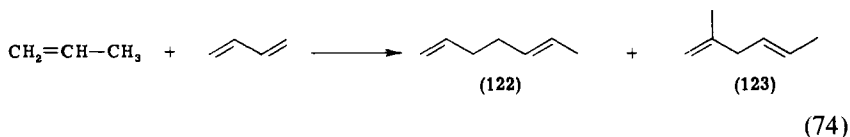


Cooligomerization of butadiene with ethylene to form 1,4-hexadiene (**120**) was carried out by Schneider using a catalyst system of $\text{PdCl}_2/\text{AlEt}_2\text{Cl}$ /phosphine (*105*, *106*). Further studies on the reaction catalyzed by a system of Pd salt/Lewis acid/phosphine without using a reducing agent were carried out by Ito and Takami (*107*). Thus, using π -allylpalladium chloride, aluminum chloride, and PPh_3 as a catalyst system, the cooligomerization was carried out in nitrobenzene at 60°C, and 1,4-hex-

adiene (**120**) was obtained in 58% yield. 1,4-Hexadiene, the primary product, was isomerized to 2,4-hexadiene (**121**) by the same catalyst.



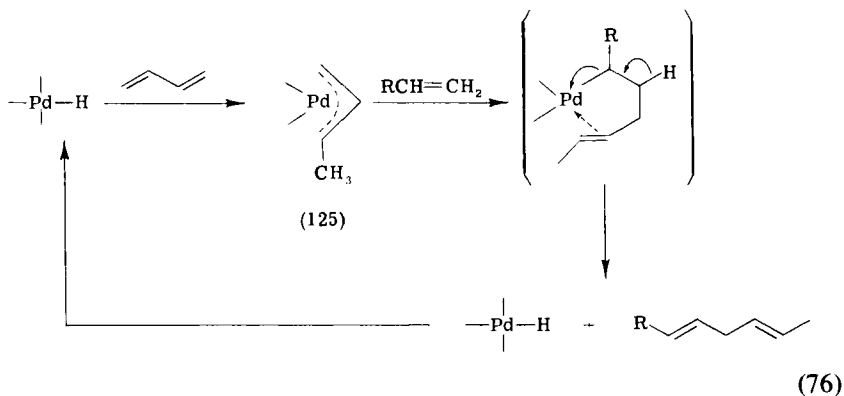
In addition, the cooligomerization of butadiene with propylene by using the same catalyst in nitrobenzene afforded 2,5-heptadiene (**122**) and 2-methyl-1,4-hexadiene (**123**) (108, 109). The ratio of the linear oligomer changed with the kind of phosphine used. Triphenyl phosphite gave the higher ratio of the linear oligomer than PPh_3 .

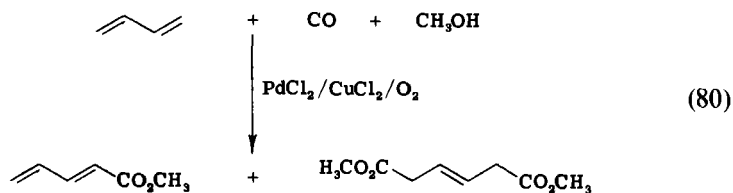


Linear cooligomerization of butadiene with styrene using π -allylpalladium chloride and BF_3 complex of PPh_3 as a catalyst at 100°C in nitrobenzene or dichloromethane produced 1-phenyl-1,4-hexadiene (**124**) (109):



These cooligomerization reactions can be explained by the following mechanism. First, insertion of butadiene to palladium hydride gives the methyl-substituted π -allylpalladium complex **125**. Subsequently, insertion of the olefin to the unsubstituted side of the π -allyl system and β -elimination give the 1,4-hexadiene and palladium hydride:

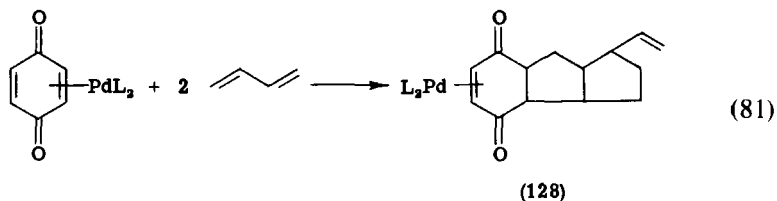




X

OTHER REACTIONS

The following unusual cyclization took place by the reaction of *p*-benzoquinone coordinated by palladium with two moles of butadiene at 60°C to give the tricyclic compound, **128** (117).



XI

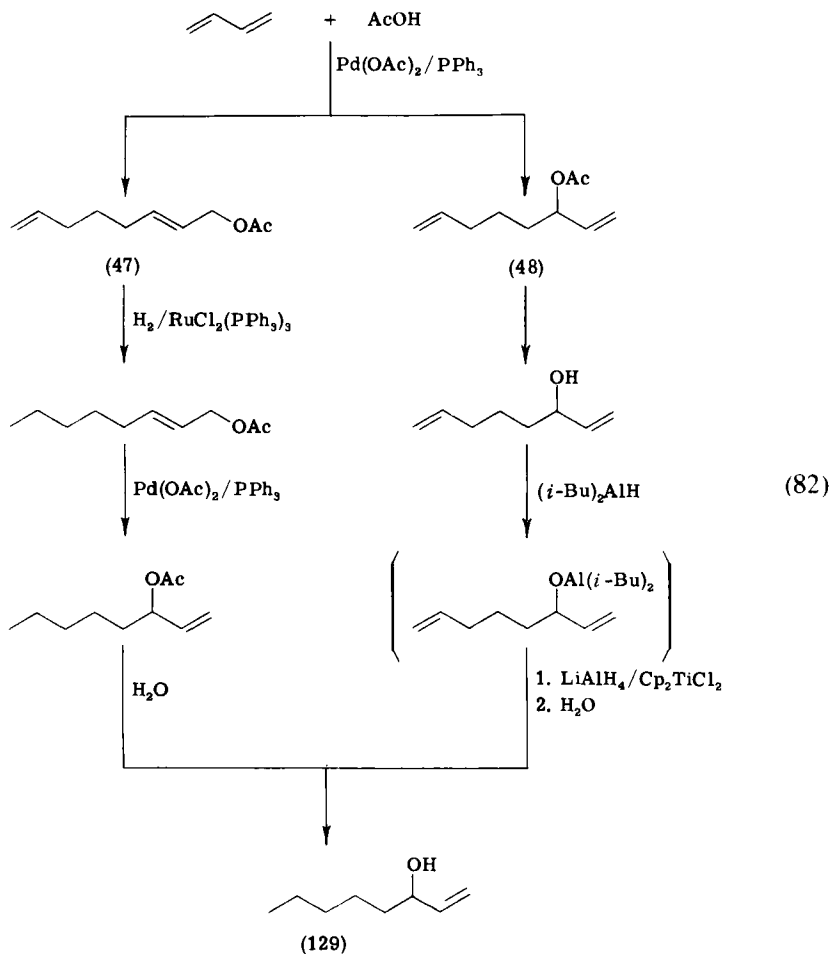
APPLICATION OF THE TELOMERIZATION OF BUTADIENE TO NATURAL PRODUCT SYNTHESIS

Various telomers and oligomers now available by the palladium-catalyzed reactions of butadiene with various nucleophiles are very useful compounds for organic synthesis, because these compounds have functional groups at one end and terminal double bonds at the other end. Several natural products have been synthesized from the telomers.

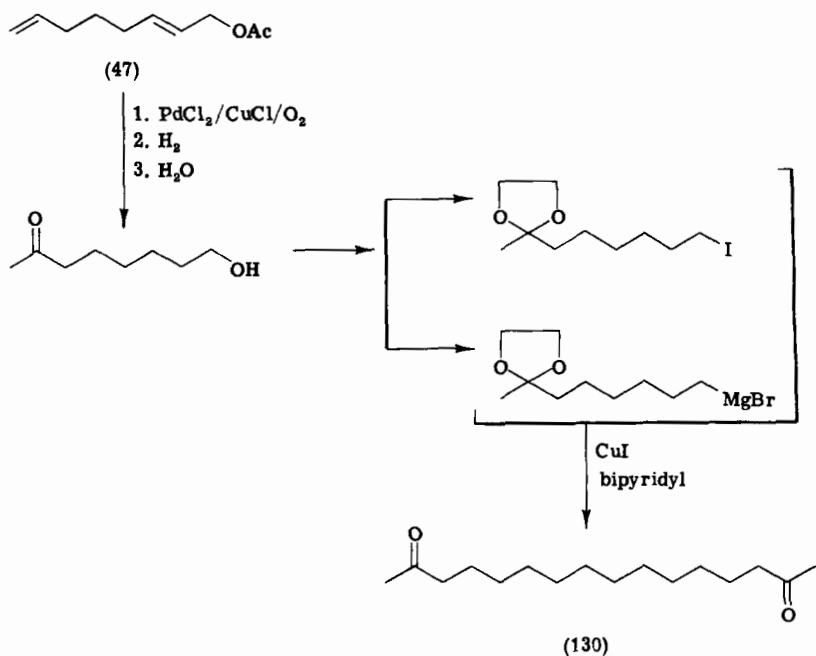
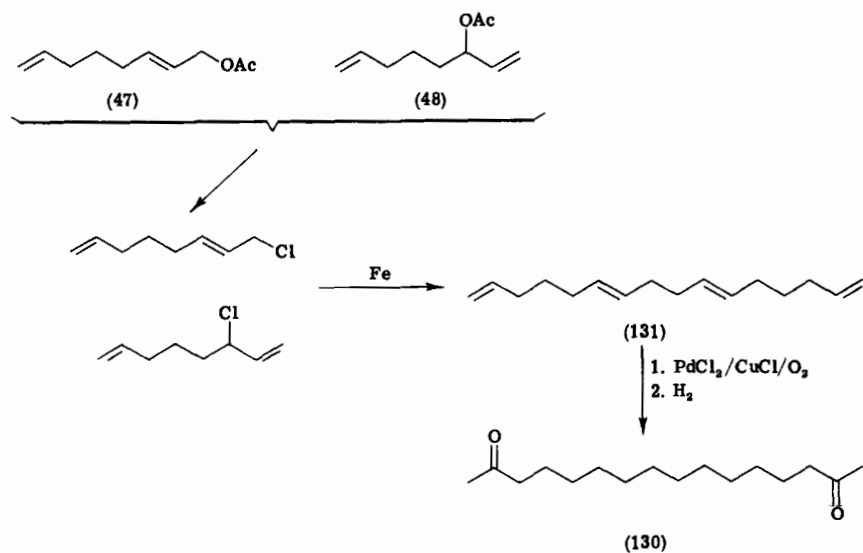
A. Uses of Acetoxyoctadienes

Acetoxyoctadienes **47** and **48** are suitable starting materials for the synthesis of 1-octen-3-ol (Matsutake alcohol) (**129**), a fragment component of a Japanese mushroom. The synthesis has been accomplished by two methods. In one method, the terminal double bond of **47** was hydro-

generated selectively using $\text{RuCl}_2(\text{PPh}_3)_3$ as a catalyst. Then the allylic rearrangement catalyzed by $\text{Pd}(\text{OAc})_2/\text{PPh}_3$ produced the acetate of 1-octen-3-ol (118, 119). In the second method, highly selective reduction of the one terminal double bond at C_7 in **48** without attack of the other terminal double bond at C_1 was carried out by a hydroalumination reaction using a titanium catalyst. The alcohol was protected as diisobutylaluminum alkoxide by treatment with diisobutylaluminum hydride. This protecting group also blocks the neighboring terminal double bond. Then LiAlH_4 was added in the presence of dicyclopentadienyltitanium dichloride as a catalyst. Hydrolysis of the product gave 1-octen-3-ol (**129**) with high selectivity (120).



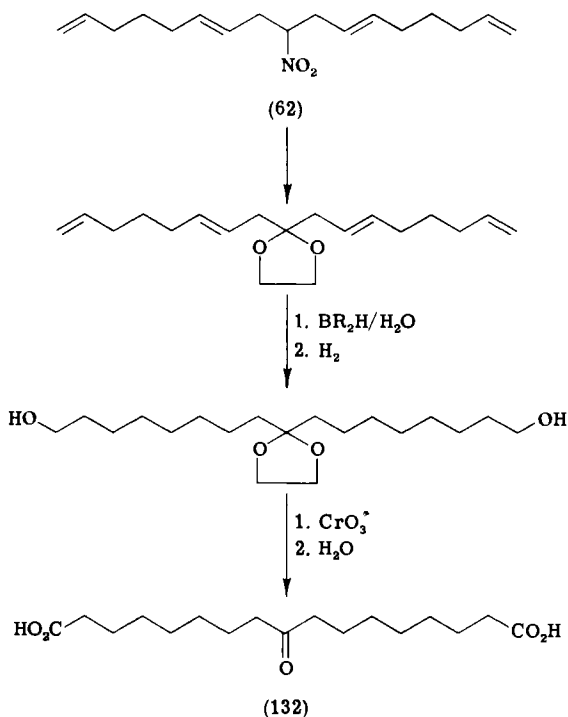
2,15-Hexadecanedione (130), from which muscone was prepared by intramolecular aldol condensation (121), was synthesized by two methods.



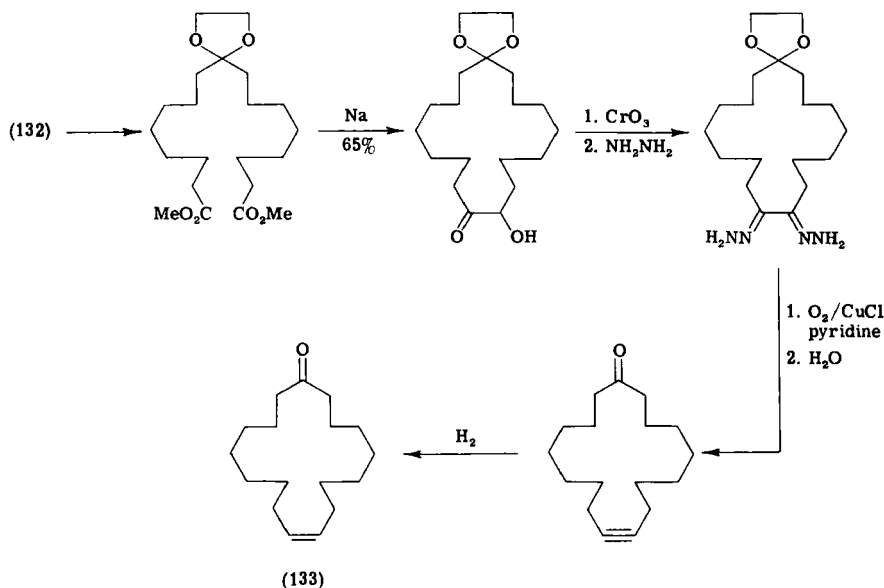
One method involved coupling of the octadienyl chain. Acetoxyoctadienes **47** and **48** were converted to corresponding allylic chlorides. A mixture of linear and branched 16-carbon tetraenes was obtained by the allylic coupling promoted by iron powder. The linear hexadecatetraene **131** as a main product was separated by distillation from isomers. The oxidation of the terminal double bonds of the tetraene with a catalyst system of $\text{PdCl}_2/\text{CuCl}/\text{O}_2$, followed by hydrogenation of the remaining internal double bonds, produced 2,15-hexadecanedione (**130**) (*122*). In another method, **47** was oxidized with $\text{PdCl}_2/\text{CuCl}/\text{O}_2$ to methyl ketone. The acetoxy group was converted to iodide and Grignard reagent, the coupling of which, catalyzed by CuI/bipyridyl , afforded the diketone **130** (*123*).

B. Uses of the Telomers of Nitroalkanes

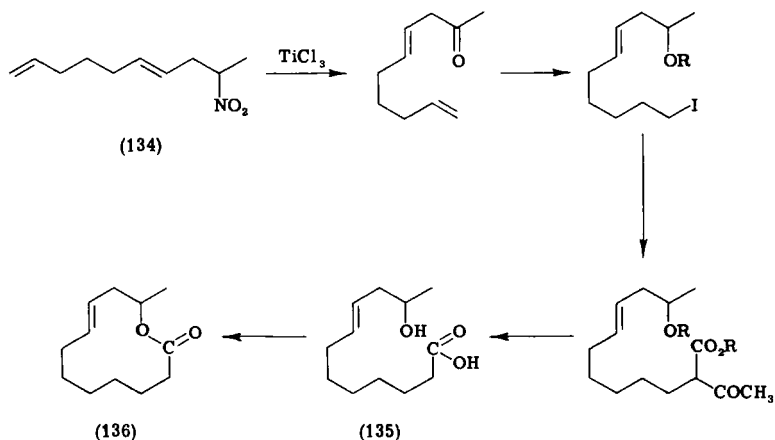
The telomer of nitromethane with four moles of butadiene **62** has a chain of 17 carbons, and this compound is a very suitable starting material with right carbon numbers and necessary functionalities for the synthesis of civetone (**133**), a naturally occurring fragrant compound. The telomer was converted into civetonedicarboxylic acid (**132**) by the following sequence of reactions:



Civetonedicarboxylic acid was then converted into *cis*-civetone (**133**) by acyloin condensation and the following steps (124):

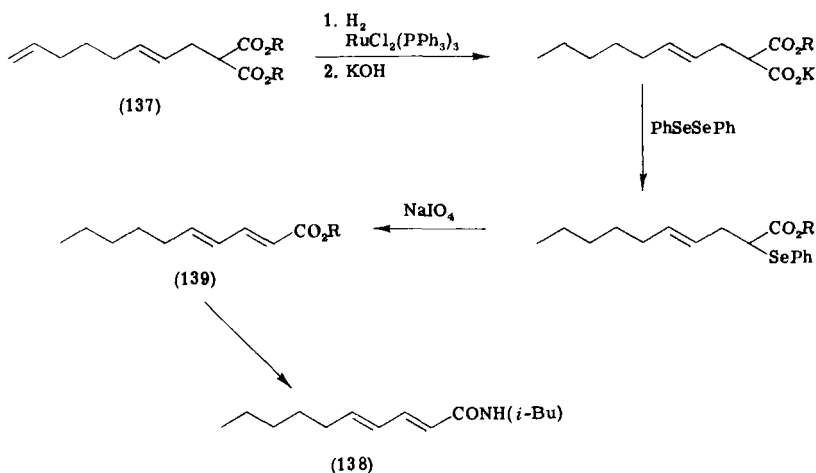


The telomer of nitroethane, **134**, was used for the synthesis of 11-hydroxy-8-*trans*-dodecenoic acid (**135**) (125). Apparently, the internal double bond of **134** must have a *trans* configuration from a mechanistic consideration. The nitro group was converted to alcohol via ketone, and the two-carbon homologation was carried out from the terminal double bond. This acid is converted to recifeiolide (**136**), a naturally occurring macrolide.

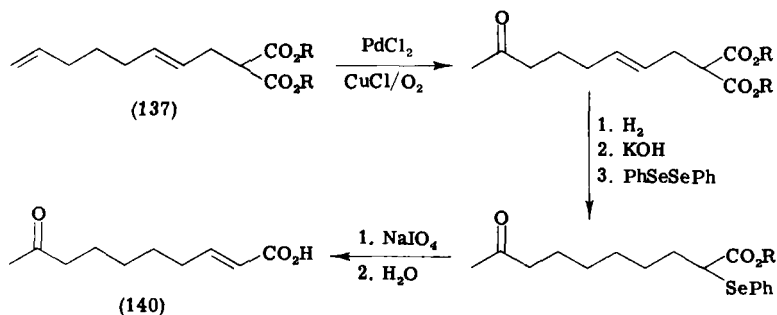


C. Uses of the Telomers of Malonate and Acetoacetate

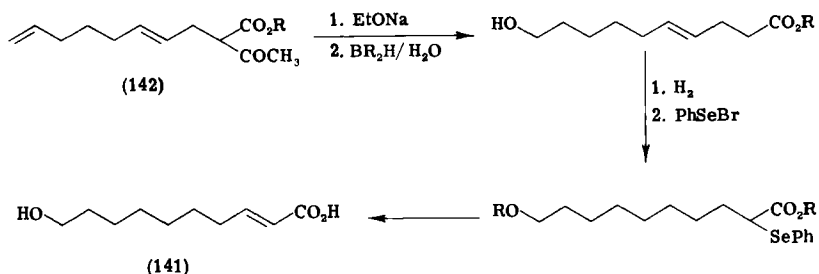
Another useful compound is the 1:2 telomer of malonate and butadiene, **137**. The first example is the synthesis of pellitorine (**138**), a naturally occurring pesticide (*126*). The terminal double bond was hydrogenated selectively with $\text{RuCl}_2(\text{PPh}_3)_3$ as a catalyst. Partial hydrolysis afforded the monoester, which was treated with PhSeSePh to displace one of the carboxyl group with phenylselenenyl group. Oxidative removal of the phenylselenenyl group afforded 2,4-decadienoate (**139**), which is converted to pellitorine (**138**):



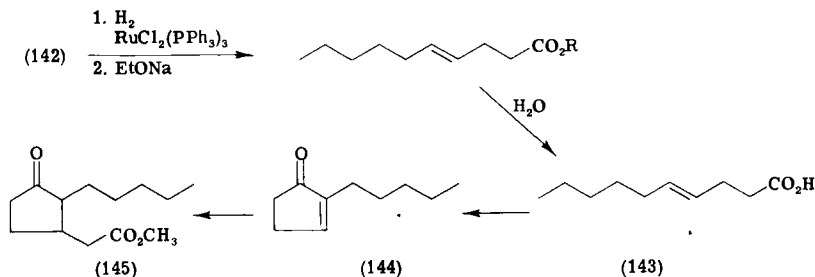
Queen substance (**140**) was synthesized from the same telomer **137** (*127*). The PdCl_2 -catalyzed oxidation of the terminal double bond produced the methyl ketone. Reduction of the internal double bond was followed by partial hydrolysis and the displacement of the carboxyl group with phenylselenenyl group, which was removed to produce queen substance (**140**):



One of royal jelly acids (10-hydroxy-2-decenoic acid) (**141**) was prepared from the telomer of acetoacetate, **142** (*128*). The terminal double bond was converted to terminal alcohol by hydroboration. The internal double bond was reduced and then reintroduced at the conjugated position by the addition of phenylselenenyl group, and its oxidative removal completed the synthesis:



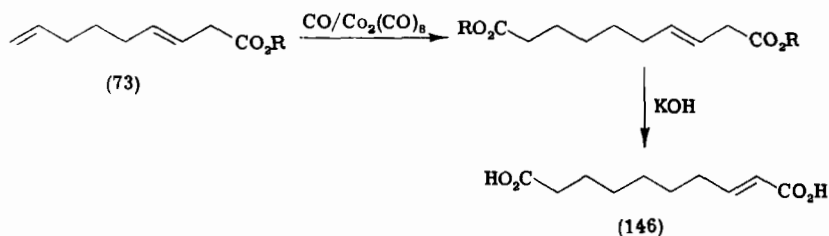
4-Decenoic acid (**143**), easily prepared from the same telomer **142**, was cyclized via acid chloride using AlCl_3 to give 2-pentyl-2-cyclopentenone (**144**). Michael addition of methyl malonate followed by removal of one ester group produced methyl dihydrojasmonate (**145**) (*129*):



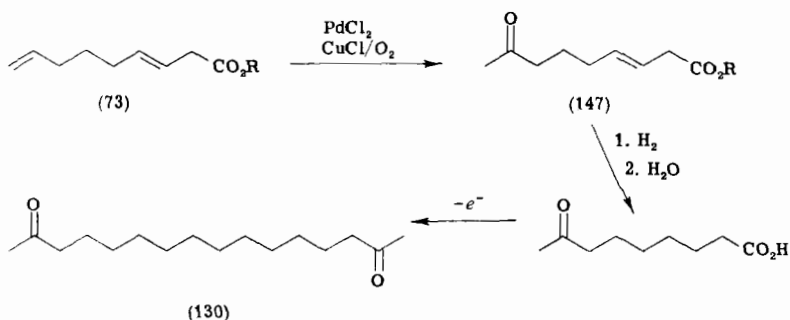
D. Uses of Nonadienoate

3,8-Nonadienoate (**73**) is used for the synthesis of another royal jelly acid, 2-decenedioic acid (**146**) (*130*). The terminal double bond was carbonylated with $\text{Co}_2(\text{CO})_8$ coordinated by pyridine. Linear ester was obtained in 80% selectivity. Hydrolysis and double-bond migration promoted by strong base produced royal jelly acid (**146**) as a crystalline compound.

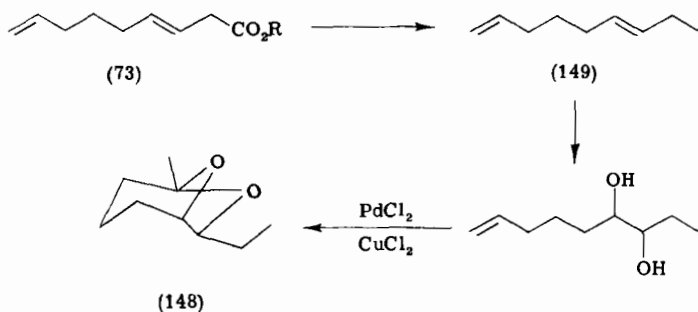
Nonadienoate was used for the convenient synthesis of 2,15-hexadecanedione (**130**) (*131*). The terminal double bond was oxidized to methyl ketone **147** with PdCl_2 , and the internal double bond was reduced. Hy-



hydrolysis of the ester produced 8-oxononanoic acid, which was then subjected to Kolbe electrolysis, and the dione **130** was obtained in high yield:



Another elegant use of nonadienoate is the synthesis of a pheromone called brevicomin (**148**) (132). The ester was converted to 1,6-nonadiene (**149**). The terminal double bond was selectively converted to glycol via epoxide. The oxidation with PdCl_2 produced brevicomin directly by intramolecular oxidative acetal formation.



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Synthetic Applications of Organonickel Complexes in Organic Chemistry

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I

INTRODUCTION

This review is an attempt to rationalize the main reaction patterns observed so far in organonickel chemistry. Synthetic work in organic chemistry has found an exceedingly valuable tool in the use of nickel complexes. The reason for this lies in the fact that nickel possesses a very favorable combination of properties to meet the requirement for an organic reaction to take place via coordination. Let us consider, for example, which basic steps occur when organic ligands react on a transition metal to form C—C bonds.

The first step is carbon-metal bond formation via coordination. This process may be followed by one or more steps, leading to transformation of ligands and/or reaction between ligands. In a final step, the metal is removed from the organic moiety. Reactions are catalytic or stoichiometric, depending on whether or not the metal is eliminated in its original oxidation state. The following is a broad classification of these processes.

(a) *Initial* (C—M bond formation): Metallacycle formation; hydride transfer or ligand protonation; C—C bond breakage; oxidative addition to R—X bonds (X = halides, or other leaving groups; R = organic group);

nucleophilic attack at coordinated ligands; electrophilic attack at coordinated ligands.

(b) *Intermediate* (transformation of the organic chain): Insertion; replacement; rearrangement; fragmentation.

(c) *Final* (metal elimination): H elimination; H addition; nucleophilic attack at the metal-bonded organic chain; electrophilic attack at the metal-bonded organic chain.

Each step includes elementary acts that require different properties of the metal, for example, sufficiently low ionization potential to favor oxidative addition, sufficiently weak metal-carbon bonds, tendency to form square-planar complexes and to reach pentacoordination to allow insertion, a sufficiently high electron affinity to allow reductive elimination, and so on. Some properties are conflicting and a compromise has to be reached.

The various properties of nickel combine in such a way that all three steps indicated above often occur without difficulty. The main limitations have been found in working with saturated substrates in direct C—H activation. So far the organonickel chemistry mainly relates to unsaturated and aromatic substrates.

For both catalytic and stoichiometric reactions, each step of the process taking place on the metal can be influenced by the nature of ligands, cations, anions, or solvent. The effects of these factors on reaction rate, selectivity, stereoselectivity, etc. cannot be easily predicted, because each step can be influenced in different ways. The reader is referred to the literature cited below.

Coordination requires vacant sites (coordinative unsaturation) (1) or facile ligand substitution. The trans and cis effect of ligands on substitution reactions has been discussed (2). Equilibria between free ligands and complexes have been studied, and information about the steric and electronic effects of ligands is available (3).

Oxidative addition is strongly influenced by donor ligands and by anionic charge of the complex, as well as by electron-withdrawing groups in the substrates (4).

Insertion is favored by ligands having a trans-labilizing effect or able to induce the correct stereochemistry of the complex with the reacting groups in mutual cis position (5). The site of attack of the migrating group on the substrate is strongly influenced by ligands (6).

Strict geometric requirements have allowed the achievement of asymmetric syntheses (7). Reductive elimination is favored by ligands which stabilize the low oxidation state of the metal (8).

Solvents affect reactions in many ways, for example, by influencing

the polarity of the medium, by selectively coordinating cations or anions, and by acting themselves as ligands (9).

The way by which all the factors involved influence the course of a reaction varies from case to case, and prediction is largely empirical. For catalytic processes, the actual species acting as catalyst is often unknown because coordination number, type of ligands, stereochemistry of the complex, and formal charge are difficult to establish in the reaction medium. Often many species are present, and the most active may be the one having the lowest coordination number and being present in a concentration so low that it cannot be detected spectroscopically. Only kinetic studies can provide evidence for such species.

The purpose of this review is to provide the reader with a scenario of what can be accomplished with nickel complexes. It is useful to do this via a series of broad schemes, hypothetical in some cases, which show the main reaction patterns, without considering mechanistic details. Examples will illustrate the various processes, but extension to other substrates or to different conditions often requires use of alternative ligands or solvents, or a change from a neutral complex to a cationic or anionic species, as indicated above. For references to syntheses with nickel see Baker *et al.* (10). For criteria for the synthesis of coordination compounds and stability of organotransition metal complexes in general, see references (11, 12). Organometallic literature has been collected periodically by Bruce (13).

For each group of reactions, different categories are distinguished, depending on the type of intermediates promoting reaction. Thus, among coupling reactions we shall distinguish between those which are hydride-, alkyl-, or aryl-promoted, and those initiated by oxidative addition of organic halides to nickel, or by replacement of halide ions in nickel halides with organic groups.

Only the general pattern of these reactions is described. In many cases the actual course of a reaction has not been elucidated, but for our purposes, the general schemes which are presented offer the opportunity to consider synthetic applications from a unified point of view. The schemes are broad in nature and possibly include some reactions still to be found. Examples illustrating the schemes do not cover the entire subject. They have been selected to provide evidence for the extensive nature of the field, particularly in the synthesis of natural products or of unusual molecules. Reactions leading to metal complexes and not to organic products have been excluded. Reactions occurring under mild conditions are naturally preferred. Reported yields, and the complexes employed, refer to the underlined references cited in the tables.

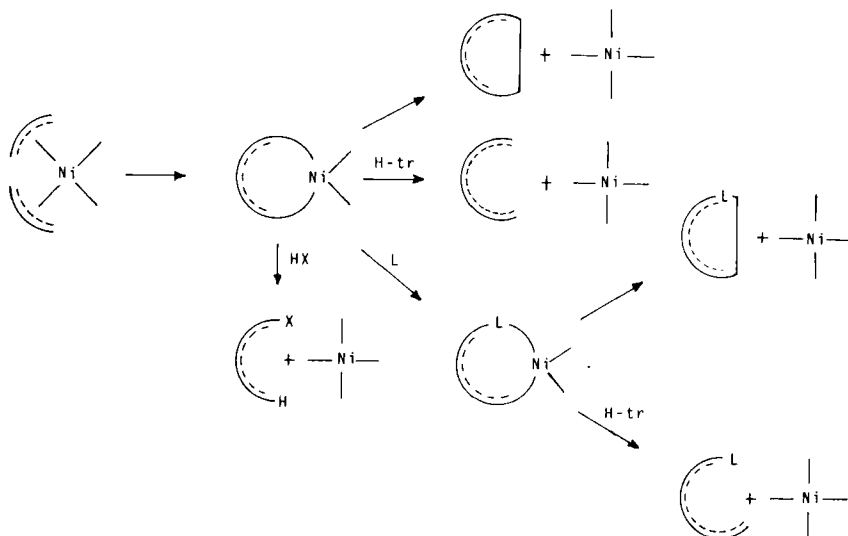
II

CARBON-CARBON BOND FORMATION¹

A. Not Affecting Functional Groups

1. Coupling of Organic Groups via Metallacycles

In the first example of coupling via metallacycles, unsaturated ligands, e.g., acetylene, ethylene, butadiene, allene, etc. (indicated in Scheme 1 by bent lines) couple by oxidative addition to zero-valent nickel, forming a metallacycle. The degree of unsaturation thus decreases by two. Dashed lines indicate that unsaturation may persist in the metallacycle. Alternatively, saturated compounds having strained rings may give a similar but saturated metallacycle. The latter can subsequently evolve in various ways: (a) It can form a cyclic compound by reductive elimination; (b) hydride transfer can occur with formation of an open, unsaturated chain; (c) another ligand can be inserted, and the metallacycle thus formed can give rise to a cyclic structure or to an open chain as before; and (d) a



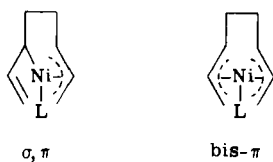
SCHEME 1. C—C coupling.

¹ Abbreviations: L = ligand, X = halogen, t = trans, c = cis, bpy = bipyridyl, CDT = cyclododecatriene, COD = cyclooctadiene, acac = acetylacetonate, AN = acrylonitrile, and DPE = bis(diphenylphosphine)ethane.

compound with mobile hydrogen can open the metallacycle either favoring path (b) above or adding to the organic chain.

Scheme 1 is illustrated by the following examples (see also Table I), which can all be interpreted as involving oxidative addition to zero-valent nickel leading to metallacycles.

The first examples of metallacycles originate with Reppe, who used nickel cyanide as a catalyst for the tetramerization of acetylene. It was later recognized that zero-valent nickel is the true catalyst. Ligands strongly affect the stereochemistry and the site of C—C bond formation of these reactions. For example, butadiene easily trimerizes to *trans,trans,trans*-cyclododecatriene with nickel complexes, containing easily replaceable olefin ligands, but in the presence of phosphines or phosphites cyclic dimers are formed (examples 3–6, Table I) (10c, n, 16–21). Among the latter, vinylcyclohexene is the major product if tricyclohexylphosphine is used, while cyclooctadiene and divinylcyclobutane are favored when tris(*o*-phenyl)phenyl phosphite is employed. In both cases the optimum ligand:nickel ratio is 1. This behavior has been attributed to the ability of the more basic phosphine ligand (L) to stabilize a σ,π -metallacycle, whereas the phosphite ligand stabilizes the bis- π -allyl form (10c);
















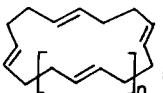
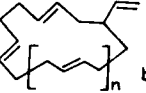





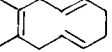

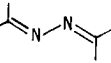
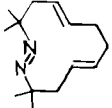



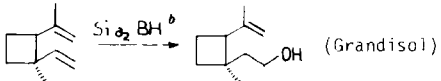

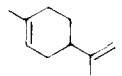
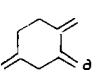
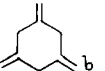
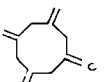





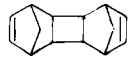


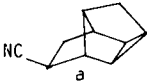
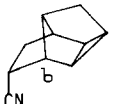


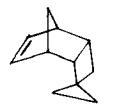

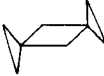



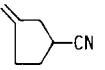
Attempts to rationalize the role of ligands in these reactions and in the even more intriguing case of cooligomerizations have been successful only in part. Steric and electronic effects of the substrate should not be considered without taking in account both the other ligands present and the oxidation state of the metal. Donor substrates are generally best stabilized by acceptor ligands and vice versa (10c), in accordance with the electroneutrality principle.

A recent approach used by Heimbach regards each C—C coupling process as a heteroring closure to which Woodward–Hoffmann rules can be applied. Regioselectivity in cyclooligomerization can be predicted on the basis of the least electron density in the LUMO of the double-bond carbon atoms of an inserting olefin (6).

Another example of the very subtle effect of a ligand is provided by the dimerization of norbornadiene (31, 52). With $(\text{PPh}_3)_2\text{Ni}(\text{CO})_2$, under irradiation, the *exo,trans,exo* dimer is formed stereoselectively (example


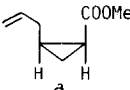
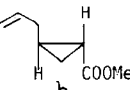

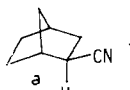
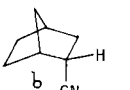
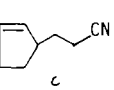

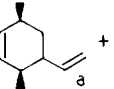
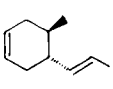
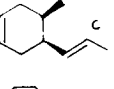
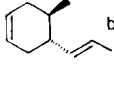


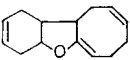
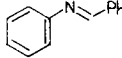
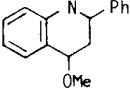

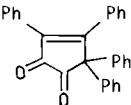

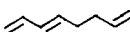

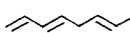


TABLE I
COUPLING VIA METALLACYCLES






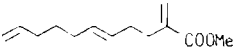


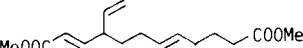


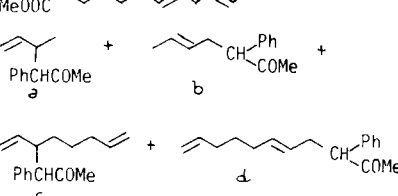

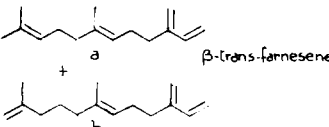

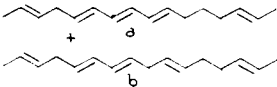



Ex. no.	Reagents	Products	Complex ^a	Yield (%)	Ref.
1		 + 	$(PPh_3)_2Ni(CO)_2$	a = 88 b = 12	14
2		 + 	$Ni(CN)_2$	a = 90	15
3			$Ni^0/P(Ph-C_6H_4)_3$	95	16-18
4			$Ni(CDT)$ or $Ni(COD)_2$	90	17, 19, 20
5			Ni^0/PCy_3	40	16
6			$Ni^0/P(Ph-C_6H_4)_3$	36	16, 17, 21
7		 + 	$Ni(\pi-C_3H_5)_2 + \pi-C_3H_5NiCl$ or $Ni(acac)_2AlEt_3 \cdot \text{CH}_2=CH-CH_2Cl$	a = 10 b = 2 for n=2	22
8	 , 		$Ni(CDT)$	80	17,23
9	 , 		Ni^0PPh_3	90	17,24
10	 , 		Ni^0PPh_3	93	25

11			$\text{Ni(COD)}_2 / \text{P(} \text{O-} \text{C}_6\text{H}_5 \text{)}_3$	15	26
12			$(\text{CDT})\text{Ni/PCy}_3 + \text{CO}$	90	27
13	$\equiv \equiv$	 a +  b +  c	$\text{Ni(CO)}_2[\text{P(Ph)}_3]_2$	a = 27 b = 8 c = 6	28
14	$\equiv \equiv$, $\equiv \equiv$	 a +  b	Ni(acac)_2	a = 45 b = 5	29
15	$\equiv \equiv$, $\equiv \equiv$	 a +  b	$[\text{P(Ph)}_3]_2 \text{Ni(CO)}_2$	a = 17 b = 26	29
201 16		 exo, trans, exo	$\text{Ni(PPh}_3)_2(\text{CO})_2 \text{ h}\nu$	29	30,31
17	 c , 	 a +  b	Ni(AN)_2 or Ni(COD)_2	a = 25 b = 25	32
18	 , 		$\text{Ni(COD)}_2/\text{PPh}_3$	86	33
19		 + 	Ni(COD)_2	45	34
20	 , 	 CN	Ni(AN)_2	82	10 1,35

(Continued)

TABLE I—(Continued)

Ex. no.	Reagents	Products	Complex ^a	Yield (%)	Ref.
21	 , $\text{CH}_2=\text{CHCOOMe}$	 + 	$\text{Ni}(\text{AN})_2$	a = 65 b = 35	36
22	 , $\text{CH}_2=\text{CHCN}$	 +  + 	$\text{Ni}(\text{AN})_2$	a = 46.5 b = 28 c = 16	37
23	 , $\text{CH}_3\text{CH}=\text{CHCH}=\text{CHCOOMe}$	 +   + 	$\text{Ni}(\text{acac})_2/\text{PPh}_3/\text{AlEt}_3$	a = 57.2 b = 2.8 c = 60 b = 30	38
24	 , 		$\text{Ni}(\text{acac})_2$ + Promoter	—	39
25	 , $\text{CH}_2=\text{CHOMe}$		$\text{Ni}(\text{CO})_4$	—	40
26	 , $\text{Ph}_2\text{C}=\text{C}=\text{O}$		$\text{Ni}(\text{CO})_4$	83.4	41
27			$\text{NiH}(\text{BH})_4(\text{PCy}_3)_2$ MeOH	60	10n,42,43
28			$\text{Ni}(\text{PPh}_3)_2\text{Br}_2$ 2 NaBH ₄	90	10n,44
29			$(\text{Bu}^n)_2\text{P}_2\text{NiBr}_2$ Bu^nLi 25 MeOH	90	45

30	 , 		Ni(CDT)	54.3	23
31	 , 		Ni ⁰	—	10n
32	 , 		Ni(acac) ₂ P(OPh) ₃ AlEt ₃	85–90	46
33	 , 		2Ni(acac) ₂ 3PhP(OPr ¹) ₂ 4PhONa	a = 13.5 b = 17.1 c = 3.6 d = 55.8	47
34			π-C ₃ H ₅ NiCl As(<i>n</i> -Hexyl) ₃ 1.2 BuOK	a = 19.1 b = 3.9	48
35			Ni(OPr ¹) ₃ AlEt ₃	a = 85.5 b = 12.5	49
36	PhCH=CH ₂	PhCH=CHCH(Me)Ph		89	50
37	CH ₂ Br ₂ , 		Ni(COD) ₂ / 2 PPh ₃	56	51

^a Ni⁰ means nickel prepared *in situ* by reduction of nickel salts, or a Ni⁰ complex containing easily displaceable ligands. ^b Disiamylborane.

^c Quadricyclane can be employed in place of dicyclopentadiene with which it is in equilibrium.

16, Table I). Codimerization of this dimer with norbornadiene also gives preferentially one stereoisomer, the *exo,trans,exo,trans,exo* isomer (30).

An example of the application of the metallacycle reaction to the synthesis of natural products is given by the synthesis of an intermediate for grandisol starting with isoprene (example 11, Table I).

It is interesting to note that Diels–Alder-type reactions (example 23, Table I) occur in a different and stereoselective way in the presence of a nickel catalyst (38). This fact strongly supports the hypothesis of metallacycle intermediates.

As shown in Scheme 1, metallacycles can be ring-opened by hydrogen transfer, generally brought about with the aid of compounds (HX) having mobile hydrogen-like acids, amines, etc. In some cases the HX compound adds to the organic chain.

This behavior is illustrated in Table I by the linear oligomerization of dienes, and the cooligomerization of dienes and olefins (examples 27–35). The H transfer may also lead to a cyclic structure (reaction 29, compared with examples 3, 5, and 6 in Table I).

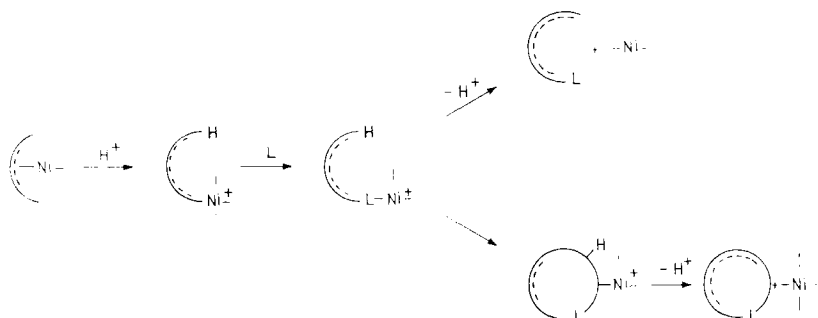
The basicity of phosphorus-containing ligands and their ability to dissociate to give sites for attachment of the double bonds of the substrate play an important role in determining the type of product formed. Another mechanism, based on formation of nickel hydrides, is available, however, for oligomerization and polymerization, as we shall see later.

The reaction of olefins with dihalogenomethanes to form homologs with one additional carbon atom has been included in the list (no. 37) of reactions in Table I because CH_2X_2 should form a carbenoid methylenenickel bond able to give a metallacycle with the olefin, followed by hydrogen transfer.

Recently, the heterogenization technique has allowed more-selective reactions to be observed. For example, butadiene gives 95% of 1,3,6-octatriene (example 28 in Table I) on a catalyst obtained by reduction of $\text{NiBr}_2(\text{supported phenylphosphines})_2$ with NaBH_4 (44). Nickel–carbonyl complexes have also been supported on phosphinated silica (53).

2. Proton- or Hydride-Promoted Reactions

The reactions covered in Scheme 2 are initiated by protonation but a hydride could form on the metal as intermediate. In some instances, cationic metal hydrides have been shown to be actually involved. See, for example, the addition of $[\text{HNi}\{(\text{POEt})_3\}_4]^+$ to butadiene (54) or of $[\text{HNi}(\text{Ph}_3\text{P})_3(\pi\text{-C}_3\text{H}_5)]$ to olefins (10c, Vol. II, p. 25). Thus the reaction of olefins or dienes with acids in the presence of zero-valent nickel may be considered proton-promoted as well as hydride-promoted.

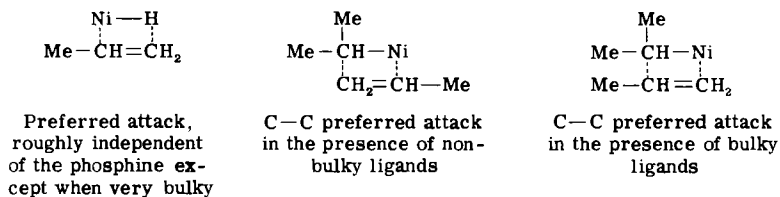


SCHEME 2. C—C coupling.

Scheme 2 shows in a simplified way protonation of an unsaturated ligand L, followed by insertion of a new ligand. The intermediate thus formed can lose a proton, forming an open-chain olefinic or unsaturated compound, or a ring can be closed, followed by hydrogen loss. Examples are reported in Table II (7, 54–67). It should be pointed out, however, that in some cases mechanisms involving metallacycle formation followed by hydrogen transfer with ring-opening cannot be excluded.

Formation of most dimers and polymers of olefins and dienes appears to be hydride-promoted (10c).

The effect of phosphorus ligands on regioselectivity of these reactions has been thoroughly studied (10c) in the case of propylene dimerization. The results show that a nickel-hydride intermediate first reacts with coordinated propylene, hydrogen preferentially attacking the terminal carbon of the double bond. The site of attack is not strongly influenced by ligands unless they are very bulky, in which case the direction of attack tends to invert. The nickel-bonded σ -alkyl group then attacks a second molecule of propylene, and in this case the direction of addition is very sensitive to steric hindrance:



Butadiene–ethylene dimerization (example 3, Table II) has been shown to proceed via a crotyl–nickel complex formed by protonation (54). It should be observed at this point that it cannot be excluded that linear cooligomerization of butadiene with ethylene to give 1,4,9-decatriene

TABLE II
HYDRIDE-PROMOTED REACTIONS

Ex. no.	Reagents	Products	Complex	Yield (%)	Ref.
1	=	+ +	Ni(PCl ₃) ₄ : AlBr ₃ : Bu ⁿ Li [0.25:5:7.5]	a = 2.5 b = 69 c = 28	55
2	≡, COOMe		Ni(CO) ₂ (PPh ₃) ₂	80	14, 56
3	, =	+ + + +	(PBu ₃ ⁿ) ₂ NiCl ₂ : Bu ₂ ⁱ AlCl [1:6]	61.5	54, 57
4		+ +	(CH ₂ =CH ₂)Ni[P(OC ₆ H ₄ -o-Me) ₃] ₂ : HCl [1:0.8]	a = 57 b = 15.4 c = 4.6	58
5		+ +	(PBu ₃ ⁿ) ₂ NiCl ₂ : Bu ₂ ⁱ AlCl [1:4]	50	59
6		+ +	(CH ₂ =CH ₂)Ni[P(OC ₆ H ₄ -o-Me) ₃] ₂ : HCl [1:0.8]	a = 53.7 b = 9.1 c = 5.1	60
7		CH ₂ OH +	(CH ₂ =CH ₂)Ni[P(OC ₆ H ₄ -o-Me) ₃] ₂ : HCl [1:0.8]	a = 67 b = 6	61

8			$(\text{PBU}_3^{\text{''}})_2\text{NiBr}_2 : \text{Bu}'\text{ONa}$ [1:1]	63	62
9			$(\text{PBU}_3^{\text{''}})_2\text{NiBr}_2 : \text{NaBH}_4 + \text{Pr}'\text{NH}_2$ [2:1]	69.2	63
10			$\pi\text{-C}_3\text{H}_5\text{NiBr} : \text{Et}_3\text{Al}_2\text{Cl}_3 : \text{PMe}_3$	93	64-66
11			$\pi\text{-C}_3\text{H}_5\text{NiCl} : \text{Et}_3\text{Al}_2\text{Cl}_3 : \text{PR}_3$ [1:2.5:1.2] $\text{PR}_3 =$ (-)-isopropyldimethylphosphine	a = 49.3 b = 13.4 O.P.(a) = 77.5	7
12			$\pi\text{-C}_3\text{H}_5\text{NiCl} : \text{Et}_3\text{Al}_2\text{Cl}_3 : \text{PR}_3$ [1:2.5:3.8] $\text{PR}_3 =$ (-)-isopropyldimethylphosphine	O.P. = 70	7, 67
13			$\pi\text{-C}_3\text{H}_5\text{NiCl} : \text{Et}_3\text{Al}_2\text{Cl}_3 : \text{PCy}_3$	35-40	64

involves the same pattern as 1,4-hexadiene formation. It was listed in Table I (example 30) as an illustration of Scheme 1 because it seems more likely that it is initiated by a metallacycle than by proton addition. Chelating phosphines can be used to prevent formation of the metallacycle, thus driving the reaction toward formation of 1,4-hexadiene (68). The mechanistic problem has not, however, yet been settled. Dissociable ligands appear to favor the metallacycle (see also Section III,C).

Polymerization reactions of olefins and dienes cannot be treated here in detail. Knowledge of the early steps which occur on nickel, as in oligomerization reactions, help explain the course of polymerization reactions and particularly their stereospecific character, as in Ziegler-Natta polymerization.

Table II also lists several isomerizations and skeletal rearrangements (examples 4-7) which are related to butadiene-ethylene dimerization. Protonation of phosphorus-containing nickel(0) complexes is sufficient to achieve skeletal rearrangement of 1,4-dienes in a few seconds at room temperature, probably via cyclopropane intermediates (example 6, Table II). For small ring rearrangements see Bishop (69).

Codimerization of butadiene with dicyclopentadiene (example 8, Table II) was shown to proceed via a crotyl-nickel complex (62). Ring contraction of cyclooctadiene (example 10, Table II) appears to be a hydride promoted reaction. The hydride-promoted dimerization of norbornadiene to *exo*-tolylnorbornene (example 9, Table II) appears to be quite different from dimerization via a metallacycle (see Table I, example 16).

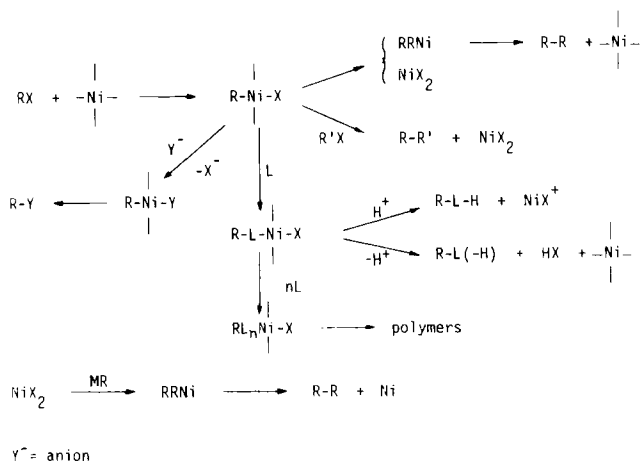
Other examples from Wilke's group are given in (examples 11-13), leading to highly stereoselective reactions, which have been exploited for asymmetric syntheses in the presence of appropriate asymmetric ligands. This subject requires separate review, however, and will not be treated further here. The reader is referred to the review by Bogdanović (7).²

3. Oxidative Addition and Replacement Reactions

Scheme 3 refers to oxidative addition of organic halides or derivatives thereof to zero-valent nickel, and to replacement reactions on Ni(II) complexes.

Oxidative addition occurs readily with allylic halides. Donor ligands (tertiary phosphines, bipyridyl, halide ions) and anionic complexes are required for activation of aromatic and vinyl halides (4, 70). Certain aliphatic halides are also reactive. The intermediate species $R-Ni-X$

² See the third article in this volume.



SCHEME 3. C—C coupling.

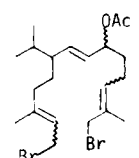
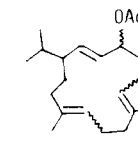
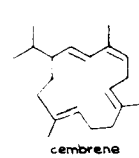
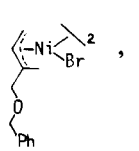
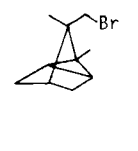
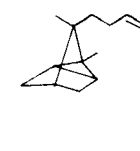
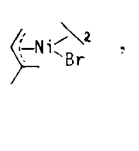
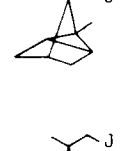
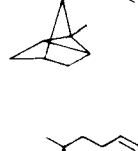
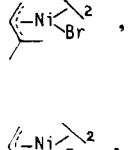
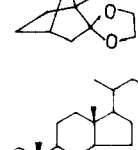
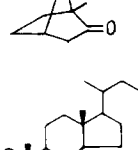
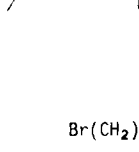
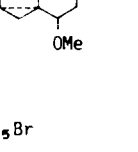
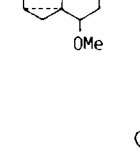
thus formed can give rise to coupling products by disproportionation and reductive elimination or by reaction with another $R'X$ molecule. Alternatively, it can insert a new ligand L , then take up or eliminate a proton. Another possibility is offered by replacement of X with a carbanion (from alkylmetal reagents or from carbon acids). A dialkyl intermediate leading to coupling of alkyl groups can also be formed by reaction of nickel halides with alkylmetals, for example with Grignard reagents. Radical processes have been detected in some cases (71).

Examples are given in Table III, relating to coupling, replacement, and insertion reactions (72–119).

Let us first examine coupling reactions of organic halides or their derivatives leading to formation of nickel(II) species. The first reaction of this kind (Table III) with tetracarbonylnickel was described in 1943 in an I G Patent. A similar reaction of allylic acetates was later reported (120). Stereoselective coupling with tetracarbonylnickel was observed as far back as 1963 (Table III, example 2). Only two of the three possible stereoisomers were obtained from the reaction of allyl halides having electron-withdrawing substituents on the double bond. Thus, with a 3-cyano substituent, the *cis,cis* and *cis,trans* coupling products (1,8-dicyano-2,7-octadienes) were formed along with very little amounts of the *trans,trans* isomer. It was postulated that one of the two moieties gave a π -allylnickel complex and the other acted on the first one. Cross-coupling reactions in which two different substrates are used have been described by Corey *et al.* (78–80, 83), who largely used homo- and cross-coupling techniques for the synthesis of natural products. Table III re-







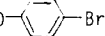
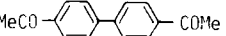
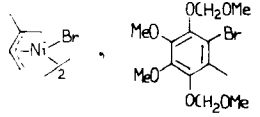
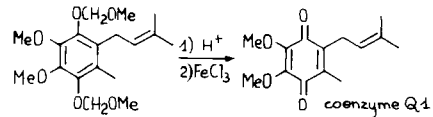
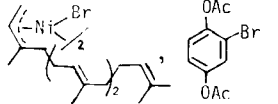
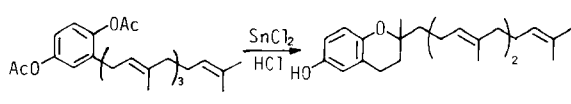
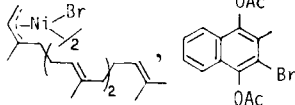
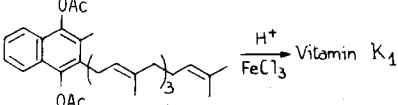
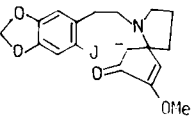
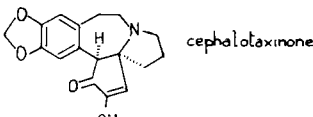
TABLE III
REACTIONS PROMOTED BY OXIDATIVE ADDITION OR BY REPLACEMENT





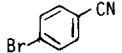
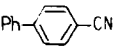

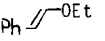
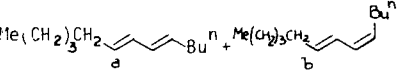

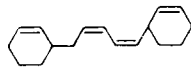

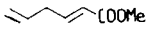
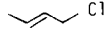
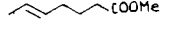
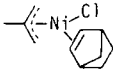
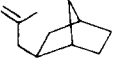

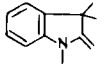
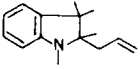
Ex. no.	Reagents	Products	Complex	Yield (%)	Ref.
1			Ni(CO) ₄	—	72
2	NC-	NC- _a + NC- _b	Ni(CO) ₄	a = 14.7 b = 31.3	73
3	, Br-	_a + _b	—	a = 57 b = 3	74, 75
4	,	 tt:tc:ct:cc = 1:0.14:0.95:0.9	—	63	75, 76
5	MeO- ,	$\xrightarrow{H^+}$	—	58	77
6		$\xrightarrow{h\nu}$	Ni(CO) ₄	—	78
7		\rightarrow	Ni(CO) ₄	63–68 ^a	79
8		\rightarrow	Ni(CO) ₄	32	80

9				Ni(CO)_4	25 ^b	81
10				—	18 ^c	82
11				—	88	83
12				—	80	84
13				—	65	85
14	$\text{Br(CH}_2)_5\text{Br}$	$(\text{CH}_2)_5$		$\text{Ni(COD)}_2/3\text{bpy}$	83	86

(Continued)

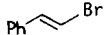

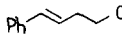
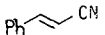
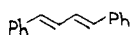
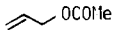
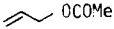

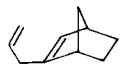
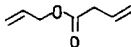
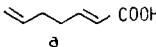
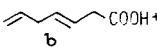
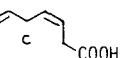
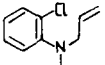

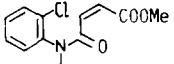
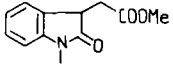
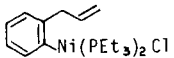


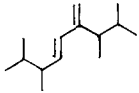
TABLE III—(Continued)

Ex. no.	Reagents	Products	Complex	Yield (%)	Ref.
15	bpyNi  , CH ₂ Cl ₂				87
16	CH ₂ Br ₂	CH ₂ =CH ₂	Ni(COD) ₂ /3bpy	58	86
17	MeOOC  Br	MeOOC  COOMe	Ni(COD) ₂ /2PPh ₃	99	88
18	PhBr, 	Ph 	Ni(CO) ₄	60	89
19	MeCO-  -Br	MeCO-  -COMe	Ni(COD) ₂	93	90
20		 coenzyme Q ₁	—	57	91
21			—	86	92
22		 t:c=8:2 Vitamin K ₁	—	44	93
23		 cephalotaxinone	Ni(COD) ₂	30	94

24	 , MeMgBr		NiCl ₂ (PPh ₃) ₂	a = 47 b = 40	95
25	 , PhMgJ		Ni(acac) ₂	70	96-98
26	 , PhZnCl		Ni(PPh ₃) ₄	90	99
27	EtO  Zr(Cl)Cp ₂ , PhJ		Ni(PPh ₃) ₄	99	100
28	Me(CH ₂) ₃ CH ₂ CH=CHAlBu ₂ ¹ , J-CH=CHBu ⁿ	Me(CH ₂) ₃ CH ₂ CH=CHCH=CHBu ⁿ + Me(CH ₂) ₃ CH ₂ CH=CHCH=CHBu ⁿ 	Ni(acac) ₂ 2 AlH(Bu ¹) ₂ 4 PPh ₃	70	101
29	PhBr , Li ⁺ CH ₂ -CO-Ph	PhCH ₂ COPh	Ni(PPh ₃) ₄	65	94, 102
30	PhBr , BrZnCH ₂ COOEt	PhCH ₂ COOEt	Ni(PPh ₃) ₄	67	103
31	PhBr , PhC≡CH , MeONa	PhC≡CPh	Ni(PPh ₃) ₄	99	104
32	 Ni-Br , ≡		—	25	105
33	 , ≡-COOMe		Ni(CO) ₄	60	106
34	 , ≡COOMe		NiCl ₂ ·6H ₂ O Fe + Thiourea	92	107
35	 , H ₂		—	83	108
36	 , 		NiCl ₂ ·6H ₂ O + Mn	52	109

(Continued)

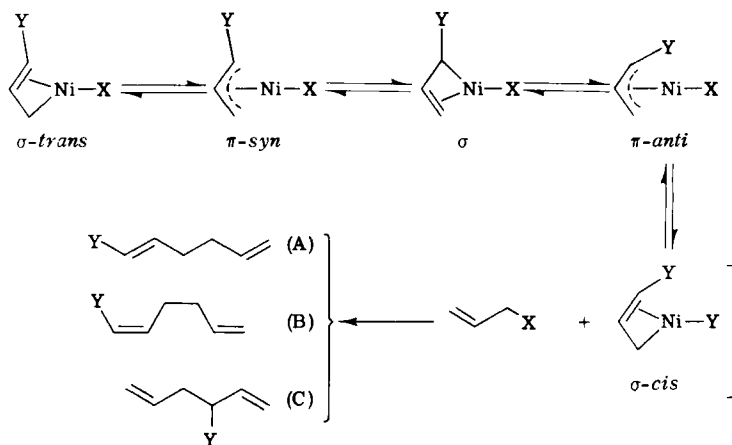
TABLE III—(Continued)

Ex. no.	Reagents	Products	Complex	Yield (%)	Ref.
37	 , 	 a +  b +  c	$K_4[Ni_2(CN)_6]$	a = 56.5 b = 30.7 c = 5.2	110
38	 , $PhC\equiv CH$	$PhC\equiv CCH_2CH=CH_2$	$Ni[P(OPr^i)_3]_4$	93	111
39	 , 		$Ni[P(OPr^i)_3]_4$	60	112
40		 a +  b +  c	$Ni[P(OPr^i)_3]_4$	a = 24.3 b + c = 48.7	113
41			$Ni(PPh_3)_4$	45.6	114
42			$Ni(PPh_3)_4$	70.5	115
43			—	58	116
44	$PhMgBr$, $CH_2=CH_2$	$PhCH=CH_2$	$NiCl_2$	45	117
45	$Me(CH_2)_6CH_2MgBr$	$Me(CH_2)_5CH=CH_2$	$NiCl_2$	63	118
46	$Pr^iCHC\equiv CH$, Bu^i_3Al 		$Ni(mesal)_2$	76	119

^a 7% of other stereoisomers are also formed.^b Including other stereoisomers.^c 27% of trans isomer is also formed.

ports several examples (reactions 5–13). The desired products, e.g., vitamin K, tokol, coenzyme Q, elemol, and santalene, are generally obtained via subsequent steps. A masked bromoketone (the enol ether of bromoacetone) has been used by Hegedus to introduce a ketonic group (example 5, Table III).

Solvent, ligand, and substituent control of stereoselectivity of reaction product between 1-carbomethoxy or 1-cyanoallylnickel halides and allyl halides has also been reported (75). Allyl halide attack at the coordinated allylic group occurs at the unsubstituted end of the latter when noncoordinating solvents are used, and at the substituted end with dipolar aprotic solvents. The latter favor solubilization of the nickel halide formed, and halide ions probably give rise to carbanionic allylnickel species. Accordingly, addition of halide ions in aprotic dipolar solvents leads selectively to the branched isomer C (see below). In the former, selective conversion of the π -allylic form to a σ form (120a) leads to the linear isomer. *Cis* or *trans* double bonds are predominantly formed, depending on the type of the substituent and on the presence of ligands. Kinetic control of the *syn*–*anti* isomerization of the coordinated allyl group may favor one of the two linear isomers A or B (Y = substituent, X = halide):



Natural products containing the “isoprene” unit can be prepared in this way. Methyl farnesoates have been synthesized from geranyl halides and 1-carbomethoxyallylnickel halides (example 4, Table III).

Vinylic halides or vinyl–metal species couple with a very high degree of stereospecificity, *cis*-vinylic halides giving *cis* coupling products and *trans*-vinylic halides *trans* coupling products (example 17, Table III). Aromatic halides give homo- or cross-coupling reactions (examples 18 and 19, Table III).

Saturated halides do not react easily in coupling reactions, although oxidative additions on nickel complexes have been observed. Some recent examples report reactions of α,ω -aliphatic dihalides with bipyridyl Ni(0) complexes leading to cycloaliphatic compounds (examples 14 and 15, Table III). Metallacycles should be formed as intermediates. A recent study by Grubbs (121) shows very interesting effects of ligands on nickel-acyclobutane complexes. One molecule of phosphine favors decomposition to 1-butene, 2 molecules give mainly cyclobutane, and 3 molecules cause splitting to ethylene. Apparently, availability of coordination sites plays an important role in these analogous reactions.

Nickel halides and nickel complexes resulting from oxidative addition can also give rise to subsequent replacement and insertion reactions. Replacement reactions have been described mainly with arylnickel halide complexes (examples 23, 29, and 31, Table III). Carbanionic species replace halide ions and can undergo coupling or insertion reactions. An example of application of a carbanionic reaction to the synthesis of a natural product is the coupling step between an aromatic iodo-derivative and an active methylene group to form cephalotaxinone (example 23, Table III).

Grignard reagents react with allylic alcohols in the presence of nickel halides to give coupling products via allylnickel complexes (example 24, Table III). Grignard reagents in general can be used to react carbanionic groups on nickel halides. Two nickel carbon bonds thus formed can easily couple, leaving zero-valent nickel. The latter can add alkyl or aryl halides, if suitable ligands are present, thus acting as a catalyst (95, 122). Many anomalies observed with Grignard reagents before the development of transition metal chemistry can be attributed to the presence of very small amounts of transition metals as impurities in the magnesium employed.

Similar coupling reactions have been achieved with other organometallic reagents such as $\text{BrZnCH}_2\text{COOEt}$ or $\text{EtOCH}=\text{CHZrCp}_2\text{Cl}$, associated with nickel (examples 26 and 27, Table III).

Acrylonitrile or methyl acrylate readily inserts into allylnickel bonds (example 34, Table III). A trans double bond is formed by loss of a proton. Insertion of acetylene followed by oxidative elimination with allyl halides gives cis double bonds (example 32, Table III). Insertion of methyl propiolate, followed by proton uptake, leads to a trans double bond (example 33, Table III). Norbornene has been shown to insert stereoselectively cis,exo into an allylnickel bond (example 35, Table III).

Attack of an allyl group on an olefin generally occurs at the terminal position; however, with trimethylmethylenindoline, this attack occurs selectively at the internal position (example 36, Table III).

Stereospecific polymerization can be initiated by allylnickel bonds:

92% *cis*-polybutadiene was obtained with allylnickel iodide (69, 123). Cationic complexes appear to favor the *cis* polymer, while neutral complexes mainly give the *trans* form.

Some of these coupling reactions can be made catalytic if hydrogen is eliminated and combines with the anion, thus leaving the nickel complex in the zero-valent state. Allylation of alkynes or of strained olefins with allylic acetates and nickel complexes with phosphites has been achieved (example 38, Table III).

If the insertion step following oxidative addition occurs on one of the two fragments resulting from oxidative addition, an intramolecular catalytic reaction ($C-O \rightarrow C-C$ rearrangement) takes place (example 40, Table III). It is interesting to note that two different products—2,6- and 3,6-heptadienoic acids—can be obtained from allyl 3-butenolate. Their ratio can be controlled by adding 1 mole of the appropriate phosphine or phosphite to bis(cyclooctadiene)nickel or similar complex. Bulky ligands favor the 2,6 isomer. It is thus possible to drive the reaction toward two different types of H elimination, namely, from the α or γ carbon atoms.

The last part of Table III catalogs examples of insertion reactions of double and triple bonds brought about by nickel complexes on other organomagnesium or aluminum species (examples 41–46).

B. Involving Direct Functionalization or Transformation of Functional Groups

1. Pseudo-Grignard Reactions


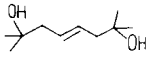

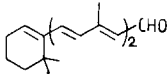
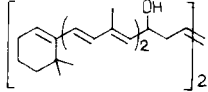

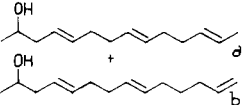

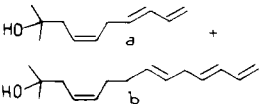

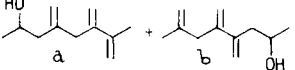

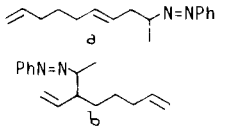

A large group of organic reactions on nickel complexes may be considered as transition metal parallels of Grignard coupling reactions. These are C—C coupling reactions involving transformation of a carbonyl group.

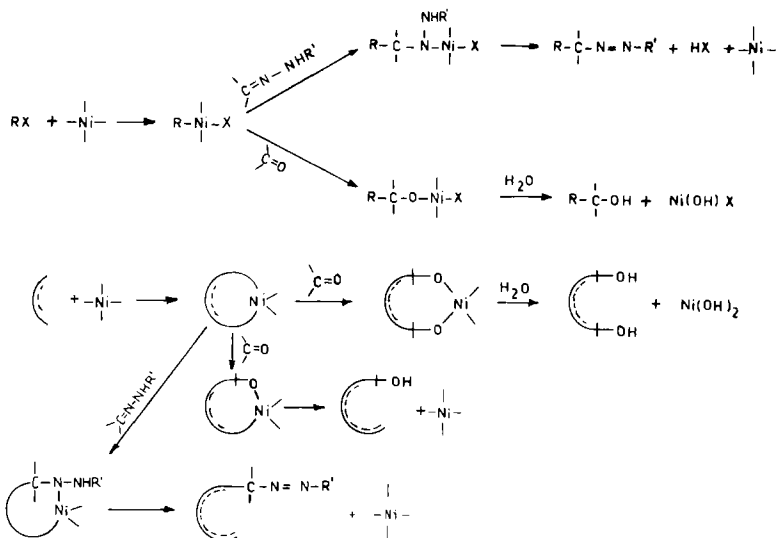
Scheme 4 indicates two general patterns. The first is based on oxidative addition of RX ($X = \text{halides or other anions}$), and the second involves metallacycle formation from unsaturated substrates. In both cases, a carbonylic compound inserts and the resulting complex is subsequently cleaved by water or protonic sources. A catalytic alternative is offered by H transfer from an acidic carbon of the organic chain to the nickel-bound oxygen. Other catalytic reactions result from use of derivatives of carbonylic functions containing an acidic hydrogen, which can be transferred to reduce the bond between nickel and the organic chain. Scheme 4 is illustrated by the data given in Table IV (83, 124–134).

The first reaction of this kind was described in 1965 (example 1, Table IV). More recently Grignard-type reactions with nickel have been carried

TABLE IV
PSEUDO-GRIGNARD REACTIONS

Ex. no.	Reagents	Products	Complex	Yield (%)	Ref.
1	$\text{Br}-\text{CH}_2-\text{CH}=\text{CH}-\text{COOMe}$, MeCOMe		$\text{Ni}(\text{CO})_4$	a = 23.3 b = 3.2	124
2	, PhCHO		—	85	83
3	, $\text{MeCOOCH}_2\text{CH}=\text{CH}_2$		$\text{Ni}(\text{COD})_2$	40	125
4	,		—	76	126
5	,		—	54	127
6	,		—	a = 26 b = 9	127
7	,		—	60	83
8	$\text{Bu}^t\text{COCH}_2\text{Br}$		$\text{Ni}(\text{CO})_4$	61	128

9	 , MeCOMe		Ni(COD) ₂	60	129
10	 , 		Ni(COD) ₂	15	129
11	 , MeCHO		—	a = 47.6 b = 8.8	130
12	 , MeCOMe		Ni(acac) ₂ P(OC ₆ H ₄ -o-Me) ₃ 5 AlEt ₃	a = 50 b = 13	131
13	 , MeCHO		Ni(COD) ₂ /PPh ₃	a = 28.1 b = 4.1	132
14	 , PhNHN=CHMe		Ni(COD) ₂ /PPh ₃	a = 69 b = 43	133
15	 , PhNHN=CH ₂	PhN=NCH ₂ CH ₂ CH=CH ₂	Ni[P(OPr ⁱ) ₃] ₄	64.2	134



SCHEME 4. Grignard-type reactions.

out in protic solvents, e.g., methanol (134a). Beside the advantage of working in methanol, there is also the possibility of having other groups in the substrate which are generally incompatible with Grignard reagents. These reactions occur with satisfactory yields using allylic acetates (example 3, Table IV). In this case, reactions are selective for aromatic aldehydes. In tetrahydrofuran solvent, ketones and aldehydes become reactive. The use of such weak ligands as triphenylarsine improves the yield, whereas stronger ligands, e.g., phosphines depress the yield, probably because they prevent coordination of the substrate. In dimethylformamide, allylnickel halides react with carbonylic compounds with good yield (example 2, Table IV). Hegedus has used a carboxy-substituted allylic halide to obtain lactones (example 4, Table IV).

Some related reactions are worth mentioning in this context. Addition of allylnickel bromide to styrene oxide to give an alcohol has been reported (example 7, Table IV). Tsutsumi has described the Darzens-type reaction of two molecules of α -bromoketones to give dimethylfurans (example 8, Table IV). This reaction consists of the addition of the ketomethylene group to the carbonyl group of another molecule, followed by epoxide formation and bromide elimination. A subsequent rearrangement leads to a dialkylfuran.

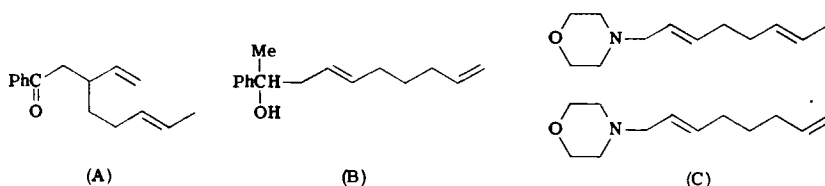
Allylnickel halides also react with quinones (example 5, Table IV).

Substitution products of the carbon-bonded hydrogen were obtained. A synthesis of coenzyme Q_1 was achieved in this way (example 6, Table IV). The site of attack in quinones is highly specific and corresponds to the noncarbonyl ring site of highest spin density of the quinone radical anion (10g, 127).

Reactions of butadiene or other dienes with aldehydes or ketones have been described by Wilke, who has applied them to several substrates, one being vitamin A (example 10, Table IV).

A study of the reactions of butadiene, isoprene, or allene coordinated to nickel in a metallacycle, with carbonylic compounds, has been reported by Baker (example 11, Table IV). In the presence of phosphines, these metallacycles adopt a σ -allyl structure on one end and a π -allyl structure on the other, as mentioned in Section II,A,1. The former is mainly attacked by aldehydes or electrophilic reagents in general, the latter by nucleophiles (C—H acids, see Table I, or amines, see Table IX).

Very subtle ligand effects have been detected in these reactions. Thus, under the same conditions, 1 mole of tricyclohexylphosphine and 1 mole of $Ni(COD)_2$ in the presence of excess morpholine catalyze addition of acetophenone to 2 moles of butadiene to give compound A below, whereas triphenylphosphine gives B. With triphenylphosphite C—C coupling no longer occurs, but morpholine adds to butadiene to give C (135).



Catalytic reactions involving addition of two molecules of butadiene and hydrogen transfer from an acidic carbon atom (adjacent to a π -allyl group) to the nickel oxygen bond were recently described (example 12, Table IV).

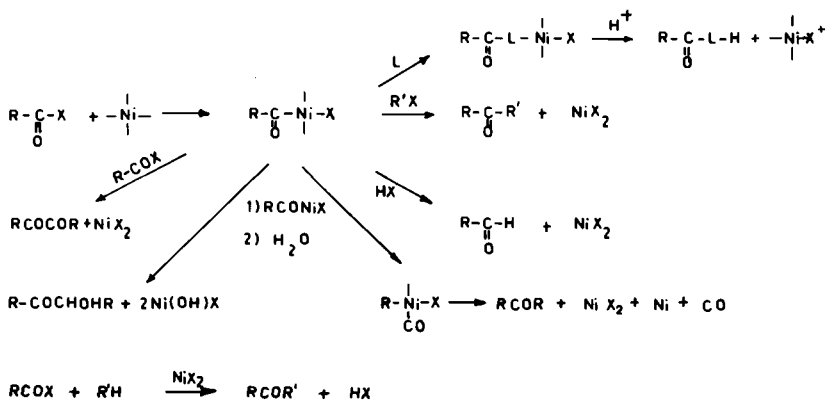
Baker has also reported the reaction of butadiene with phenylhydrazones leading to azoalkenes (example 14, Table IV). This is also a Grignard-type reaction which is catalytic. Analogous results were obtained with methylhydrazones (136). A wider scope was recently attained by causing allylic esters to react with phenylhydrazones in the presence of zero-valent nickel complexes having trialkyl phosphites (example 15, Table IV).

2. Acylation Reactions

Another group of C—C coupling reactions involve transformations of the acyl function. Thus, Scheme 5 presents simplified patterns for formation of ketones (R = alkyl or aryl group, R' = aryl, X = halide).

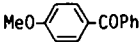

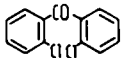
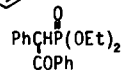
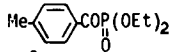
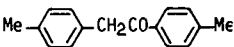
An intermediate acylnickel halide is first formed by oxidative addition of acyl halides to zero-valent nickel. This intermediate can attack unsaturated ligands with subsequent proton attack from water. It can give rise to benzyl- or benzoin-type coupling products, partially decarbonylate to give ketones, or react with organic halides to give ketones as well. Protonation of certain complexes can give aldehydes. Nickel chloride also acts as catalyst for Friedel–Crafts-type reactions.

Examples in Table V illustrate coupling, as well as electrophilic and nucleophilic additions. Both electrophilic and nucleophilic reactivity of a coordinated acyl group are possible, depending on the ligands present and the oxidation state of nickel (137–139). In the presence of triarylphosphines, benzoyl chloride reacts with methyl acrylate and zero-valent nickel to give methyl benzoylpropionate, a nucleophilic-type addition (example 3, Table V). Polarity inversion of the acyl group is an important aspect of the organonickel chemistry of the acyl group. Other nucleophilic acylations involving formation of the acylating agent by carbonylation are considered in Section II,B,4. A simple method for obtaining ketones from o -substituted aroyl chlorides was recently described (example 4, Table V). These compounds decarbonylate and give rise to ketones with good selectivity at room or lower temperature. Decarbonylation of β,γ -unsaturated acid chlorides directly gives 1,5-dienes (140). Friedel–Crafts-



SCHEME 5. Acylation.

TABLE V
ACYLATION REACTIONS

Ex. no.	Reagents	Products	Complex	Yield (%)	Ref.
1	PhCOCl	$\begin{array}{c} \text{PhC}=\text{CPh} \\ \text{PhOCO} \quad \text{OCOPh} \end{array}$	Ni(CO) ₄	40	137
2	PhCOCl, PhOMe		NiCl ₂	12	138
3	PhCOCl, CH ₂ =CHCOOMe	PhCOCH ₂ CH ₂ COOMe	Ni(COD) ₂ /2PPh ₃	33	138
4			Ni(COD) ₂ /2PPh ₃	73	138
5	PhCOP(OEt) ₂		Ni(COD) ₂	39	139
6			NiCl ₂ + Mn	40	139
7	PhCOP(OEt) ₂ , MeCOOH	PhCHO	Ni(COD) ₂	25	139

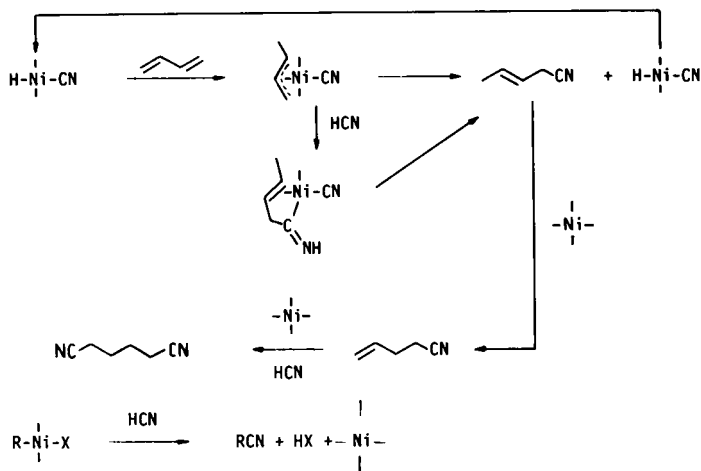
type reactions were observed with anisole and anhydrous nickel chloride (example 2, Table V).

Other syntheses of ketones and aldehydes were recently achieved, using dialkyl aroylphosphonates RCOP(=O)(OR')_2 and zero-valent nickel. Diethyl-1,2-diphenyloxyethyl phosphonate, diethyl-1,2-diphenyloxyethyl phosphate, deoxybenzoin, and benzaldehyde were formed (examples 5–7, Table V). These reactions reveal rather complex patterns. The first step is an oxidative addition of aroylphosphonate to zero-valent nickel, leading to an aroylnickel phosphonate RCONiP(=O)(OR')_2 . At this point, each of the two nickel-bonded groups, the aroyl and the phosphonic group, can migrate to another molecule of aroylphosphonate or of aroylnickel phosphonate, giving rise to C—C or C—P coupling products. An important step, frequently occurring, consists of the migration of the phosphonyl group from carbon to oxygen to form a phosphate group. When the latter is present β to a carbonylic function it can be eliminated easily by reduction with zero-valent nickel, probably because of the easy electron transmission via the carbonyl group. Elimination of the phosphate group leads to deoxybenzoin or to dialkyl diaryloxyethylphosphonates (a class not easily accessible by other ways). A direct synthesis of deoxybenzoins from benzoylphosphonates, nickel halides, and a reducing agent as Mn powder at room temperature, has been achieved (example 6, Table V).

3. Cyanation Reactions

Another important method for C—C coupling on a nickel complex involves cyanation. This reaction has been mainly studied with butadiene to obtain adiponitrile, an important precursor of nylon and is likely to be the most important industrial application of organonickel chemistry. It consists of two steps, namely, addition of HCN to butadiene to give mainly 3-pentenitrile, followed by addition of HCN to 4-pentenitrile, formed by isomerization of the 3-isomer. Internal double bonds are rather inert, and an equilibrium concentration of 4-pentenitrile suffices to form adiponitrile exclusively. The first step is catalyzed by Ni(0) complexes with phosphites; the second, including isomerization, also requires Ni(0) complexes with phosphites, Lewis acids generally being added. Allylic intermediates are very likely, but it is not yet clear whether a direct reductive elimination process of the coordinated alkyl and cyano groups is involved, or whether a new molecule of hydrogen cyanide first adds to the complex before coupling with the alkyl group as shown in Scheme 6 (141–145).

Another interesting cyanation reaction, also brought about by nickel(0)



SCHEME 6. Cyanation.

triphenylphosphine complexes, is aromatic substitution of aryl halides (146). This reaction is also catalytic and works at temperatures lower than 100°C. In this case also, the final elimination step is not completely clear. Pentacoordinated intermediates have been postulated. Vinyl halides react similarly.

Table VI reports examples of cyanation (146–150).

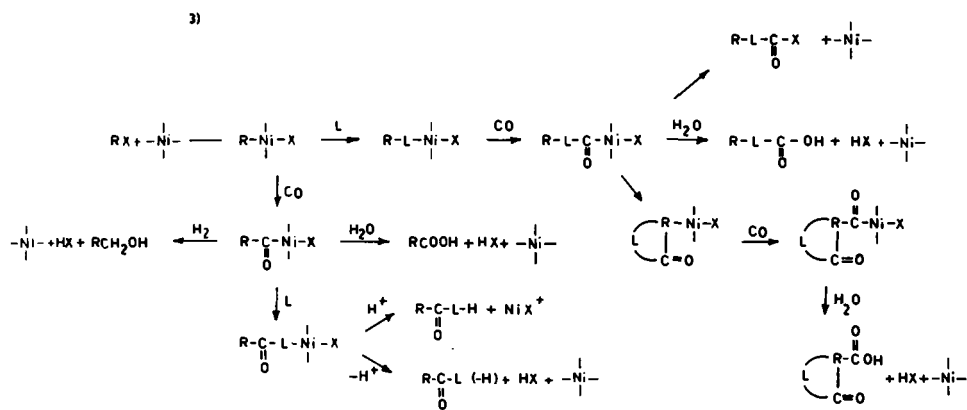
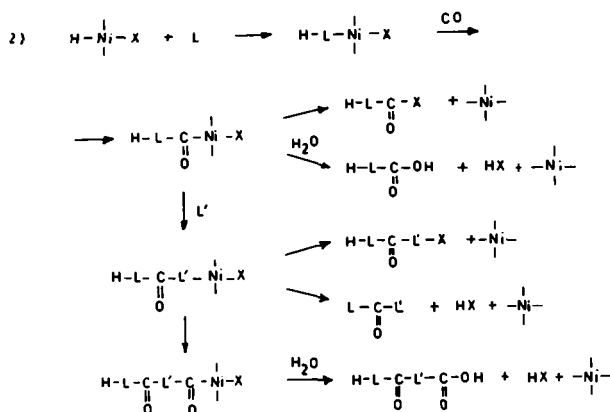
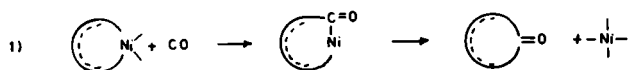
4. Carbonylation Reactions

Carbonylation is an exceedingly broad subject, but the main reaction patterns can be easily rationalized by recalling the classification used earlier for coupling reactions involving: (a) metallacycles; (b) hydride-promoted reactions; and (c) oxidative addition of organic halides to zero-valent nickel. In fact, one or other of these steps is necessary to form a species able to undergo carbonylation.

Scheme 7 comprises the following patterns: First, a metallacycle gives rise to ketones by CO insertion and reductive elimination. Next, a nickel hydride inserts an unsaturated substrate L, followed by CO. The acyl intermediate can give rise to reductive elimination with formation of acyl halides or acids and esters by hydrolysis, or it can insert a new ligand with subsequent reductive elimination as before. Alternatively, there may be a new insertion of carbon monoxide with final hydrolysis. Third, an intermediate R-Ni-X is formed by oxidative addition. It can react in several ways: It can insert a new ligand L, followed by CO to give an

TABLE VI
CYANATION REACTIONS

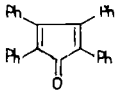

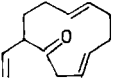

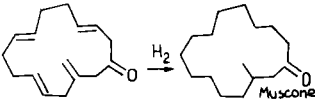
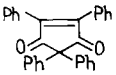

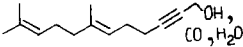
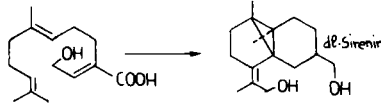
Ex. no.	Reagents	Products	Complex	Yield (%)	Ref.
1	PhBr , NaCN	PhCN	Ni(PPh ₃) ₄	95	146
2	$\text{Ph}-\text{CH}=\text{CH}-\text{Br}$, KCN	$\text{Ph}-\text{CH}=\text{CH}-\text{CN}$	K ₄ Ni ₂ (CN) ₈	78	147, 148
3	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$, HCN	$\text{MeCH}=\text{CHCH}_2\text{CN}$ _a + $\text{CH}_2=\text{CHCH}(\text{Me})\text{CN}$ _b	Ni[P(OEt) ₃] ₄	a = 52.3 b = 41.2	149
4	$\text{CH}_3\text{CH}=\text{CH}-\text{CN}$, HCN	NC(CH ₂) ₄ CN _a NCCH ₂ CH(Et)CN _b + NCCH ₂ CH ₂ CH(Me)CN _c	Ni[P(OPh) ₃] ₄ 20 P(OPh) ₃ 5 ZnHPO ₃	a = 47.2 b + c = 17.3	150

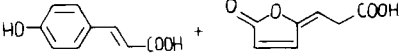

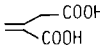
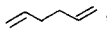
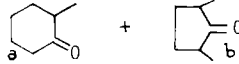
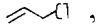

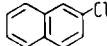
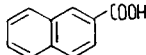



SCHEME 7. Carbonylation.

acylnickel halide. The latter can lead to reductive elimination with formation of an acyl halide or undergo hydrolysis to acids or to esters in the presence of water or alcohols, or it can cyclize (if R contains an unsaturation at the appropriate site) and insert new CO molecules before hydrolytic cleavage. Alternatively, the intermediate R—Ni—X can insert carbon monoxide, then ligand L, followed by loss or capture of a proton. Examples of Scheme 7 are provided in Table VII (10b, f, v, 17, 124, 137, 140, 147, 148, 150–192).

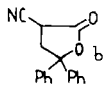

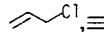
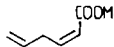
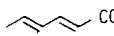
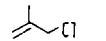
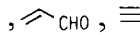
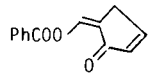

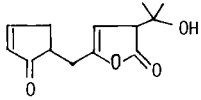
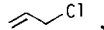
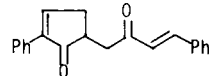
TABLE VII
CARBONYLATION REACTIONS


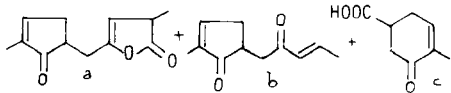




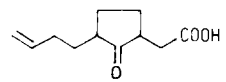

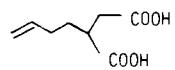


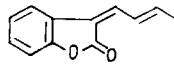


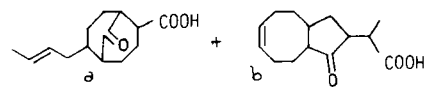


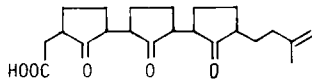
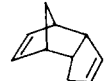

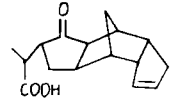


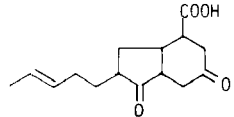
Ex. no.	Reagents	Products	Complex	Yield (%)	Ref.
1	$\text{PhC}\equiv\text{CPh}$, CO		Ni(CO)_4	—	150
2	 , CO			—	17
3	 , C_6H_6 , CO			<4 ^a	152
4	$\text{PhC}\equiv\text{CPh}$, $\text{Ph}_2\text{C}=\text{C}=\text{O}$, CO		Ni(CO)_4	12	153
5	Ph_2CN_2 , EtOH , CO	$\text{Ph}_2\text{CHCOOEt}$	Ni(CO)_4	74	154
6	$\text{HSCH}_2\text{CH}_2\text{OH}$, CO , O_2		Ni(CO)_4	60	155
7	C_6H_6 , MeOH , CO	$\text{CH}_2=\text{CHCOOMe}$	$\text{Ni(CO)}_4 + \text{HCl}$	85	156
8	 , CO , H_2O		Ni(CO)_4	30	157
9	C_6H_6 , CO , EtOH , HCl	$\text{EtOOCCH}_2\text{CH}=\text{CHCH}=\text{CHCH}_2\text{COOEt}$	Ni(CO)_4	35 ^b	158
10	C_6H_6 , CO , MeOH	$\text{CH}_2=\text{CHCOOMe}^c$	$[\text{Ni(CO)}_3\text{I}]^-$	—	159

11	\equiv , CO, H ₂ O		$[\text{Ni}(\text{CO})_3\text{I}]^-$	—	159
12	$\text{PhC}\equiv\text{CPh}$, CO, H ₂ O	$\text{PhCH}=\text{C}(\text{Ph})\text{COOH}$	$\text{Ni}(\text{CO})_4$	56	153, 160
13	\equiv , CO, MeOH		$\text{Ni}(\text{CO})_4$	62	161
14	\equiv -Cl, CO, H ₂ O		$\text{Ni}(\text{CO})_4$	46	163
15	 , CO, HCl		$\text{Ni}(\text{CO})_4$	a = 24.5 b = 45.5	164
16	$\text{Me}(\text{CH}_2)_5\text{CH}=\text{CH}_2$, CO, H ₂ O	$\text{Me}(\text{CH}_2)_5\text{CH}(\text{Me})\text{COOH}$	$\text{Ni}(\text{CO})_4$	—	165
17	$\text{CH}_2=\text{CHBr}$, CO, MeOH	$\text{CH}_2=\text{CHCOOMe}$	$\text{Ni}(\text{CO})_4$	70–80	166, 167
18	c- or t- $\text{PhCH}=\text{CHBr}$, CO, MeOH	c- or t- $\text{PhCH}=\text{CHCOOMe}$	$\text{Ni}(\text{CO})_4$	80	147, 166
19	 , CO, H ₂ O		$\text{Ni}(\text{CO})_4$	40	168
20	PhCH_2Cl , CO, H ₂ O	PhCH_2COOH	$\text{Ni}(\text{CO})_4$	95	10f, 169, 170
21	 , CO, H ₂ O		$\text{Ni}(\text{CO})_4$	97	137, 147, 171
22	$\text{Me}(\text{CH}_2)_6\text{I}$, CO, Bu^tO^-	$\text{Me}(\text{CH}_2)_6\text{COOBu}^t$	$\text{Ni}(\text{CO})_4$	66	147
23	 , CO, H ₂ O	$\text{HOOC}(\text{CH}_2)_4\text{COOH}$	NiJ_2	80	172
24	$\text{Me}(\text{CH}_2)_5\text{CH}(\text{OH})\text{Me}$, CO, H ₂ O	$\text{Me}(\text{CH}_2)_5\text{CH}(\text{Me})\text{COOH}$	$\text{Ni}(\text{CO})_4$, HCl	76	173
25	PhCH_2Br , CO	$\text{PhCH}_2\text{COCH}_2\text{Ph}$	$\text{K}_4[\text{Ni}_2(\text{CN})_6]$	90	148
26	$(\text{bpy})\text{Ni}(\text{Me})_2$, CO	MeCOOMe or MeCOCOMe^e		90	174
27	PhMgBr , PhBr , CO, H ₂ O	PhCOPh + Ph_3COH	$(\text{bpy})\text{Ni}(\text{Et})_2$	a = 30.5 b = 20.5	174
28	PhJ , p- $\text{MeC}_6\text{H}_4\text{HgCl}$, CO	p- $\text{MeC}_6\text{H}_4\text{COPh}$	$\text{Ni}(\text{CO})_4$	88	175

(Continued)

TABLE VII—(Continued)

Ex. no.	Reagents	Products	Complex	Yield (%)	Ref.
29	PhJ , $\text{CH}_2=\text{CHCN}$	$\text{PhCOCH}_2\text{CH}_2\text{CN}$ + 	$\text{Ni}(\text{CO})_4$	a = 29 b = 30	176
30	 , PhJ , CO	$\text{PhCOCH}_2\text{COPh}$	$\text{Ni}(\text{CO})_4$	91	177
31	$\text{Li}[\text{pMeC}_6\text{H}_4\text{CONi}(\text{CO})_3]$, PhCH_2Cl	$\text{pMeC}_6\text{H}_4\text{CO}\overset{\text{OH}}{\underset{\text{CH}_2\text{Ph}}{\text{C}}}\text{C}_6\text{H}_4\text{pMe}$		73	178
32	$\text{Li}[\text{Me}_2\text{NCONi}(\text{CO})_3]$, PhCOCl	PhCOCONMe_2		95.6	179
33	 , \equiv , CO , MeOH	 $\xrightarrow{\text{NaOH}}$ 	$\text{Ni}(\text{CO})_4$	74	10b, v, 168, 180
34	PhJ , \equiv , CO , MeOH	$\text{PhCOCH}_2\text{CH}_2\text{COOMe}$	$\text{Ni}(\text{CO})_4$	>90	140
35	$\text{Li}[\text{PhCONi}(\text{CO})_3]$, $\text{PhC}\equiv\text{CH}$	$\text{PhCOCH}(\text{Ph})\text{CH}_2\text{COPh}$		74	181
36	$[\text{BuCONi}(\text{CO})_3]^- \text{Li}^+$, $\text{Me}_2\text{C}=\text{CHCOMe}$	$\text{BuCOC}(\text{Me})_2\text{CH}_2\text{COMe}$		89	182
37	 , \equiv , CO	m $\text{MeC}_6\text{H}_4\text{OH}$	$[\text{Ni}(\text{CO})_3\text{J}]^-$	74	183
38	PhCOCl ,  , \equiv		$\text{Ni}(\text{CO})_4$	56	184
39	 , \equiv , MeCOMe		$\text{Ni}(\text{CO})_4$	48.3	124
40	 , $\text{PhC}\equiv\text{CH}$, CO		$\text{Ni}(\text{CO})_4$	64	185

41	$\text{MeC}\equiv\text{CH}$, CO , 		Ni(CO)_4	a = 55.7 b = 27.8 c = 46.5	185
42	 Cl, = , CO, H ₂ O		Ni(CO)_4	42	186
43	 Cl,  , CO, H ₂ O		Ni(CO)_4	10-40	186
44	 Br , CO , H ₂ O		Ni(CO)_4	60	187
45	 ,  Cl , CO		Ni(CO)_4	77	188
46	 ,  Cl , CO , H ₂ O		Ni(CO)_4	a = 6.6 b = 1.8	189
47	 ,  Cl , CO, H ₂ O		Ni(CO)_4	10-12	190
48	 ,  Cl , CO , H ₂ O		Ni(CO)_4	10	191
49	 Cl ,  , CO , H ₂ O		Ni(CO)_4	8	192
50	PhCH=CHBr , \equiv , CO , MeOH	$\text{PhCH=CHCH=CHCOOMe}^f$	Ni(CO)_4	14	166

^a 40% with alkylisonitriles in place of CO (151). ^b Estimated; the main by-product is $\text{CH}_2=\text{CHCOOEt}$. ^c $\text{MeOOCCH=CH(CH}_2)_4\text{CH=CHCOOMe}$ and $\text{MeOOCCH}_2\text{CH=CHCH}_2\text{CH=CHCOOMe}$ are also formed. ^d Methylacetylene can be used with equivalent results (162). ^e Acetone is obtained selectively at room temperature and biacetyl at -78° . ^f Trans and cis cinnamic methyl esters are the main by-products.

The first two reactions (Table VII) date as far back as 1953, to Reppe's chemistry, and refer to processes occurring via metallacycles. An interesting application to natural products is the synthesis of muscone, which, however, has been obtained in a better way using alkylisonitriles (151) in place of carbon monoxide (example 3, Table VII).

Hydride-promoted reactions are also well known, such as the acrylic and vinylacrylic syntheses (examples 7–10, Table VII). Some less-known compounds, which form in the presence of halide ions added to tetracarbonylnickel, have been described by Foà and Cassar (example 11, Table VII). Reaction of allene to form methacrylates, and of propargyl chloride to give itaconic acid (via butadienoic acid), have been reported (examples 13 and 14, Table VII). 1,5-Hexadiene has been shown to be a very good substrate to obtain cyclic ketones in the presence of hydrogen chloride and tetracarbonylnickel (example 15, Table VII). The latter has also been used to form esters from olefins (example 16, Table VII). In the presence of an organic acid branched esters form regioselectivity (193).

Vinyl halides (example 17, Table VII) were first observed by Kröper to form acrylic esters by reaction with carbon monoxide under pressure and tetracarbonylnickel in methanol at 100°C. These reactions were later shown to occur under much milder conditions. Highly stereospecific reactions were observed: *cis*-vinyl halides gave *cis*-carbonylation products and *trans*-vinyl halides *trans*-carbonylation products (example 18, Table VII). Retention of configuration of alkyl substrates in carbonylation seems to be a general feature in carbon monoxide chemistry (193a).

Allylic halides (example 19, Table VII) carbonylate under very mild conditions. An inverse effect of the CO pressure was observed in reaction with $\text{Ni}(\text{CO})_4$, CO dissociation being required to allow coordination of the substrate (168).

Organic groups can be rendered more nucleophilic toward carbon monoxide by adding halide ions. Benzyl chloride easily gives phenylacetic acid in this way (example 20, Table VII).

Aromatic halides (example 21, Table VII) also react in the presence of $\text{Ni}(0)$ complexes in alkaline media. Complex nickel carbonyl anions, such as $\text{Ni}_5(\text{CO})_{12}^{2-}$, $\text{Ni}_6(\text{CO})_{12}^{2-}$, $\text{Ni}_9(\text{CO})_{18}^{2-}$ (194) are formed which, being more nucleophilic, can attack aromatic halides.

Reactions of alcohols, ethers, and aliphatic halides with carbon monoxide were described as far back as 1948–1953 (173, 195). High pressure and temperature were required, however, for these processes. The use of alkaline media allowed carbonylation of alkyl iodides under mild conditions (example 22, Table VII). More recently, carbonylation of alkyl-nickel complexes was reported (example 26, Table VII).

Formation of acetic acid from methanol and carbonylation of alcohols still are important industrial problems, but milder conditions are needed. Other metals, such as rhodium, have proved to be more suitable.

Besides direct carbonylation, insertion of acetylene and of other molecules and groups into C—Ni bonds is possible. A variety of linear or cyclic products results. Thiourea proved an exceedingly efficient ligand (180).

Some distinctive features of the insertion reactions reported in Table VII can be summarized as follows: First, carbon monoxide gives rise by insertion (5, 195a) to acyl bonds which are easily cleaved by water, alcohols, or compounds with mobile hydrogen. The metal is thus easily removed from the organic part and, being eliminated in its reduced state, can undergo a further oxidative addition, leading to a catalytic cycle. Thus, use of CO is very favorable for catalytic reactions.

Second, insertions are very selective, and the nature of the bond between organic groups and nickel determines the type of molecule which can be inserted. For example, allylic groups prefer to react with acetylene rather than with carbon monoxide (example 33, Table VII) but the opposite is true for benzyl or aryl groups. π -Lactonyl groups do not react either with carbon monoxide or acetylene, but they do react with ketones or aldehydes (example 39, Table VII). In this way sequential reactions take place on nickel with high selectivity.

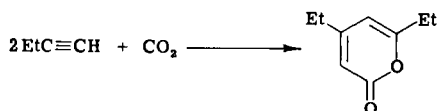
Third, if the acylnickel bond is stable enough, it can react inter- or intramolecularly with triple or double bonds (see examples 33, 41, and 46–49, Table VII). If it reacts intramolecularly it may give rise to cyclic ketones, containing the rings of cyclopentane or cyclohexane, or to phenols. The types of substrate strongly influences the ability to cyclize and the kind of ring formed. For example, a 6-membered ring leading to *m*-cresol is preferred to a methylcyclopentenone ring (example 37, Table VII); cyclopentenones easily result from the ring closure of unsaturated acyl chains (examples 38 and 41, Table VII); and α,β -unsaturated γ -ketoacyl chains easily form π -lactonyl complexes which can further react with ketones (example 39, Table VII).

Cyclopentanones form from CO and double bonds in 1,5-positions (example 43, Table VII). This is a very selective and stereoselective process, the 1,4- or 1,6-positions being not significantly reactive under the same conditions. *o*-Hydroxyphenylacetylenes also form 5-membered lactones (example 45, Table VII). In some cases ring closure leads to a new nickel–carbon bond into which a new molecule of carbon monoxide can be inserted. This process of alternative insertion of carbon monoxide and other unsaturated ligands can be repeated several times so that complex alicyclic structures can be formed (example 49, Table VII). This

may be relevant from the point of view of the syntheses of natural products or their analogs, e.g., steroids. The main difficulty lies in competition between ligands for coordination sites, but steric effects (even a methyl group can hinder the reaction) and geometric requirements are demanding. High selectivity but low yields are obtained (examples 46–49, Table VII).

A fourth feature of carbonylation is the strong influence carbon monoxide exerts on the insertion process. Ligands which normally would not be able to react are induced to react with each other by the presence of carbon monoxide, even if the latter is not inserted (196). Certain reactions, such as insertion of norbornene or dicyclopentadiene into an allylnickel bond, which normally do not proceed to a significant extent in the absence of carbon monoxide, do proceed in its presence, and with insertion of the latter. We believe that carbon monoxide, in addition to its trans effect, favors insertions by providing a final irreversible step consisting of the hydrolytic cleavage of the acyl group, which shifts to the right all the preceding reversible steps taking place on the metal.³

So far, carbon dioxide insertion has found limited use to form C—C bonds. Dialkyl pyrones have been obtained in low yield (up to 9%) from alkylacetylenes, probably via CO₂ insertion into a metallacycle (198), e.g.:



Zero-valent nickel-chelating phosphine complexes are used at 120°C under CO₂ pressure.

III

FORMATION OF BONDS OTHER THAN CARBON—CARBON

The last part of this review refers to methods for forming C—X, O—H, N—H, C—O, C—N, and certain other bonds.

Most of the general patterns of these reactions can be explained according to the scheme already shown for formation of C—C bonds. Thus, —OH, —OR, and —NR₂ additions to butadiene have been considered in Scheme 1 where HX is H—OH, H—OR, or H—NR₂.

³ It is also possible that carbon monoxide helps insertion by forming cyclometallated structures of the type shown by Floriani for acetylbis(cyclopentadienyl)methylzirconium (197).

A. Hydrogenation and Reduction

Raney nickel has long been known as a hydrogenation catalyst. Other forms of active nickel can be easily prepared by reducing nickel salts *in situ* with NaBH_4 , Fe, Grignard reagents, etc. (199–202).

Some of these reagents have been shown to be extremely selective in hydrogenating one double bond in preference to other double bonds present in the same molecule, or in reducing a triple bond selectively to a cis double bond, or in avoiding concomitant isomerization of other double bonds (examples 2–5, Table VIII) (199, 200, 203–204). Soluble $\text{Ni}_2(\text{CN})_6^{4-}$ has also been employed for hydrogenation of unsaturated compounds (214, 215). Double-bond isomerization generally accompanies hydrogenation. Certain nickel hydrides are thought to be responsible for this behavior, as shown by experiments with nickel hydride complexes containing phosphorus ligands (216, 217). It is possible, however, to achieve selective hydrogenations without appreciably isomerizing other double bonds (example 4, Table VIII). Reactions of Ni—H have been reviewed (218). Reductions of aromatic rings, and ketones (to alcohols), and nitro-derivatives, or nitriles (to amines) have been reported (examples 6–10, Table VIII).

Hydrogenolysis of organic halides is another general reaction performed by nickel complexes (examples 11 and 12, Table VIII).

Hydride transfer from organic substrates to olefins (219) or halides (220), catalyzed by halogeno(triphenylphosphine)nickel complexes, and halide replacement reactions (example 13, Table VIII) by hydrolytic cleavage of nickel complexes have also been described.

Association of sodium hydride and alkali alkoxides with nickel salts has been reported to be effective in many hydrogenations and selective reductions of organic halides (211, 221).

The use of the nickel cluster $[\text{Ni}_4(\text{CNCMe}_3)_7]$ in hydrogenation of alkynes was recently described (222, 223).







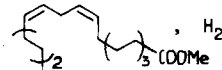
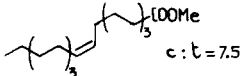


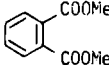
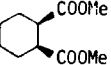
Some nickel catalysts supported on phosphinated silica were shown to be superior to their homogeneous analogs (224).




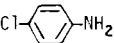


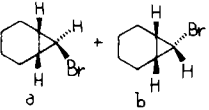



B. Oxidation and Alkoxylation

Oxidation of organic substrates with molecular oxygen on nickel complexes is limited to a few known examples.

Tertiary phosphines are oxidized catalytically by nickel(0) complexes with formation of phosphine oxides. Also, complexed *tert*-butylisocyanides can be oxidized to the corresponding isocyanates (examples 1 and 2, Table IX) (225–226).

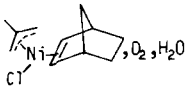
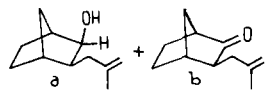
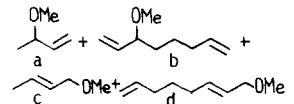
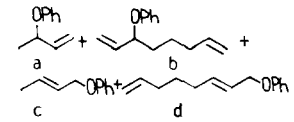
TABLE VIII
HYDROGENATION AND REDUCTION

Ex. no.	Reagents	Products	Complex	Yield (%)	Ref.
1	$\text{Me}(\text{CH}_2)_5\text{CH}=\text{CH}_2$, H_2	$\text{Me}(\text{CH}_2)_6\text{Me}$	$\text{Ni}(\text{OAc})_2 + \text{NaBH}_4$	98	200
2	 , H_2	 +  + 	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O} + \text{Fe}$	a = 54.3 b = 8.3 c = 26.5	199
3	 , H_2		$\text{NiCl}_2 \cdot 6\text{H}_2\text{O} + \text{Fe}$ $\text{Ni}(\text{OAc})_2 \cdot \text{NaBH}_4$	98 98	199 200
4	 , H_2	 c : t = 7.5	$\text{NiCl}_2 + \text{NaBH}_4$	85	203, 204
5	$\text{EtC}\equiv\text{CEt}$, H_2	 + 	$\text{Ni}(\text{OAc})_2 + \text{NaBH}_4$	a = 96 b = 3	200
6	 , H_2		$\text{Ni}(\text{Ethylhexanoate})_2 \cdot \text{AlEt}_3$ [1:3-4]	100	205, 206

7	 , H ₂		Ni(Ethylhexanoate) ₂ : AlEt ₃ [1:3-4]	100	206
8	 , NaBH ₄		NiCl ₂ (PPh ₃) ₂ + NaBH ₄	80	207
9	PhNO ₂ , NaBH ₄		"R _M CH ₂ PNi" ^a	85	208
10	MeCN , H ₂	EtNH ₂	Ni(CO) ₄	41	209
11	Me(CH ₂) ₉ Cl , LiAlH ₄	Me(CH ₂) ₈ Me	NiCl ₂ + LiAlH ₄	98	210
12			NaH·Amyl'ONa·Ni(OAc) ₂	a = 61 b = 21.5	211
13	 or  , H ₂ O		Ni(CO) ₄	99	212, 213

^a Ni supported on phosphinated styrene-divinylbenzene copolymer.

TABLE IX
OXIDATION AND ALKOXYLATION

Ex. no.	Reagents	Products	Complex	Yield (%)	Ref.
1	PPh_3 , O_2	$\text{Ph}_3\text{P}=\text{O}$	$\text{Ni}(\text{PPh}_3)_4$	— ^a	225
2	Bu^tNC , O_2	Bu^tNCO	$\text{Ni}(\text{COD})_2$	60–70	226
3	 , O_2 , H_2O			a = 32 b = 7	227
4	PhBr , PhONa	Ph-O-Ph	$\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$	33	228
5	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$, MeOH		NiBr_2 30PEt_3	a = 20.5 ^b b = 29.5 c = 18.4 d = 11.6	229, 230
6	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$, PhOH		$\text{Ni}[\text{P}(\text{OPh})_3]_4$	a = 11 ^c b = 16 c = 13 d = 60	231

^a Turnover number = 50.

^b Wt% of product.

^c Selectivity.

Oxidation of carbon ligands with concomitant insertion has been observed in the reaction of methallyl nickel complexes with norbornene or strained olefins in general and oxygen (example 3, Table IX).

Replacement of aromatic halogens with OAr groups (example 4, Table IX) seems to follow the same patterns already mentioned for other substitution reactions.

Addition of MeOH or PhOH to butadiene (examples 5 and 6, Table IX) also occurs according to previously discussed patterns.

C. Amination

Examples of amination reactions of aromatic halides and of unsaturated compounds are presented in Table X (228, 232–240).

Aromatic amination by replacement of halogens with amines (example 1, Table X) requires tertiary phosphine–nickel halide or tertiary phosphine–nickel carbonyl complexes at 140–170°C. This implies oxidative addition of aromatic halides to nickel, replacement of the halide with amines, and reductive elimination.

Reaction of amines with dienes or allenes (examples 2 and 3, Table X) should be considered within the framework of addition of HX compounds to dienes (Section II,A,1) (47, 135, 232–235, 241). It is worthwhile noting that very subtle effects of ligands have been observed in these reactions. It is rather striking, for example, that passing from di(isopropoxy)phenylphosphine to di(methoxy)phenylphosphine addition to butadiene is no longer observed (235). Probably competition between substrate and ligand is an important factor requiring easily dissociable groups. The latter probably also influences the ratio between 1:1 and 1:2 products of addition of amines to butadiene. Ligand dissociation should favor formation of the bis- π -allyl metallacycle mentioned in Section II,A,1, whereas a more tightly held ligand should favor formation of a π -crotylnickel complex (241).

Another way to enhance 1:1 addition of amines to butadiene consists of the use of catalytic amounts of protic acids, which apparently give rise to π -crotyl groups (234).

Allylation of amines with allylic alcohols in the presence of reducible nickel complexes easily occurs at $\sim 80^\circ\text{C}$ (example 4, Table X).

Carbonylations of azoderivatives, chloramines, or aldimines are other ways of achieving amination, as shown by the last three examples in Table X.

TABLE X
AMINATION

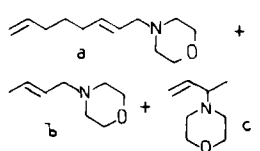
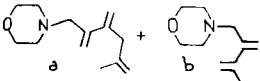
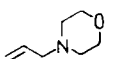
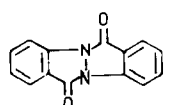
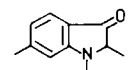








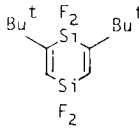
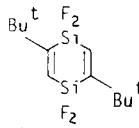


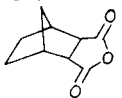

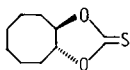

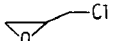
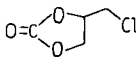
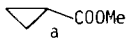
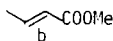

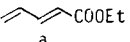
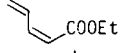
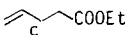
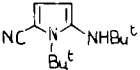
Ex. no.	Reagents	Products	Complex	Yield (%)	Ref.
1	PhBr, H-N <chem>C1CCNCC1</chem>	Ph-N <chem>C1CCNCC1</chem>	(dpe)Ni(CO) ₂	85	228
2	<chem>C=CC=C</chem> , H-N <chem>C1CCOCC1</chem>		Ni(acac) ₂ PhP(OPr ⁱ) ₂ NaBH ₄	a = 49 b = 30.7 c = 14.4	232-235
3	<chem>C=C=C</chem> , H-N <chem>C1CCOCC1</chem>		NiBr ₂ PhP(OPr ⁱ) ₂	a = 72 b = 22	236
4	<chem>C=CCO</chem> , H-N <chem>C1CCOCC1</chem>		(PBU ₃ ⁿ) ₂ NiBr ₂ Bu ^t OK	98	237
5	PhN=NPh, CO		Ni(CO) ₄	50	238
6	Bu ^t NCI ₂ , CO, H ₂ O	Bu ^t NHCONHBu ^t	Ni(CO) ₄	80	239
7	p-MeC ₆ H ₄ J, PhCH=NMe, CO		Ni(CO) ₄	60	240

TABLE XI
INTRODUCTION OF OTHER FUNCTIONS AND MISCELLANEA

Ex. no.	Reagents	Products	Complex	Yield (%)	Ref.
1	$Bu^n C \equiv C Bu^n$, $HSiCl_3$, $MeMgBr$	$Bu^n CH=C(SiMe_3)Bu^n$ _a + $Bu^n(SiMe_3)C \equiv C(SiMe_3)Bu^n$ _b	$NiEt_2(bpy)$	a = 13 b = 77	242
2	 , Me_3SiH	 _a $SiMe_3$ +  _b $SiMe_3$	$Ni(COD)_2/2AsPh_3$	a = 70 b = 28	243
3	 , $HSi(OEt)_3$	 _a $Si(OEt)_3$ +  _b $Si(OEt)_3$	$Ni(acac)_2/AlEt_3$	a = 59.5 b = 25.5	244
4	 , $HSi(OEt)_3$	 $OSi(OEt)_3$	$Ni(COD)_2$	80	245
5	$Bu^t-C \equiv CH$, $F_2Si-SiF_2$	 + 	$Ni(CO)_4$	—	246
6	 Cl , SO_2 , $MeOH$	 SO_3Me + $(\text{CH}_2)_2SO_2$ _b	$Ni(CO)_4$	a = 20 b = 23	247
7	$MeMgBr$, $(PPh_3)_2NiCl_2$, H_2O	PhH + $PhMe$ + $Ph-Ph$ + Ph_2MeP + $PhMe_2P$		—	248
8	$C_{10}H_7Cl$, $Cu(Py)_2(SNC)_2$, $KSCN$	$C_{10}H_7SCN$	$Ni(PPh_3)_3$	90	249
9	$PhCl$, $Cu(Py)_2(ONC)_2$, $KOCN$	$PhNCO$	$Ni(PPh_3)_3$	54	249
10	$PhCl$, $Cu(Py)_2(NO_2)_2$, $NaNO_2$	$PhNCO_2$	$Ni(PPh_3)_3$	70	249
11	$C_{10}H_7Cl$, $CuBr_2$	$C_{10}H_7Br$	$Ni(PPh_3)_3$	98	249
12			$Ni(CO)_2(PPh_3)_2$	53	250

(Continued)

TABLE XI—(Continued)

Ex. no.	Reagents	Products	Complex	Yield (%)	Ref.
13		 cis	Ni(COD) ₂	99	251
14	 , CO ₂		Ni(PCy ₃) ₂	100	252
15	CH ₂ N ₂ , CH ₂ =CHCOOMe	 + 	Ni(PPh ₃) ₄	a = 72 b = 7	253
16	CHN ₂ COOEt, 	 +  	—	a = 69 b = 19 c = 8	254
17	HC≡CH, Bu ^t NC		Ni(AcO) ₂	77	255
18	$\begin{matrix} \text{O}=\text{P}(\text{OEt})_2 \\ \text{Ph}-\text{C}-\text{OH} \\ \text{O}=\text{P}(\text{OEt})_2 \end{matrix}$	$\begin{matrix} \text{O} \\ \text{Ph}-\text{CH}-\text{P}(\text{OEt})_2 \\ \text{O}-\text{P}(\text{OEt})_2 \\ \text{O} \end{matrix}$	Ni(COD) ₂ /2PPh ₃	98	256
19	Ph ₃ P=CH ₂	Ph ₂ PCH ₂ Ph	Ni(COD) ₂	—	257
20	MeCH=NOH	MeCONH ₂	Ni(acac) ₂	—	200, <u>258</u>
21	m-MeC ₆ H ₄ Br, Ph ₃ P	m-MeC ₆ H ₄ PPh ₃ Br	Ni(PPh ₃)	90	259

D. Introduction of Other Functions and Miscellaneous Reactions

Among the reactions reported in Table XI, the most important from a synthetic point of view appears to be the silylations (examples 1–5), which take place catalytically with satisfactory yields.

Oxidative addition of the silyl species to nickel is followed by insertion of unsaturated substrates. Zero-valent nickel complexes, and complexes prepared by reducing nickel acetylacetonate with aluminum trialkyls or ethoxydialkyls, and in general Ziegler–Natta-type systems, are effective as catalysts (244, 260–262). $\text{Ni}(\text{CO})_4$ is specific for terminal attack of SiHCl_3 on styrene (261).

Other reactions involve formation of C—S or C—P bonds by insertion of SO_2 and by substitution at phosphorus, respectively (examples 6 and 7, Table XI).

Replacement reactions of aromatic halides or other halides with SCN, NCO, or NO_2 can be easily carried out by oxidation of nickel complexes with copper salts (examples 8–11, Table XI).

Transformation of cyclic anhydrides or thioanhydrides into *cis*-olefins also appears a synthetically useful procedure (examples 12 and 13, Table XI).

Insertion of carbon dioxide into olefin oxides gives olefin carbonates, and is an example of basic catalysis with nickel(0) complexes (example 14, Table XI).

Reactions of diazoderivatives and of *tert*-butylisonitrile probably involve the intermediacy of carbene species (examples 15 and 17, Table XI).

Examples 18–20 in Table XI refer to rearrangements involving heteroatoms.

Finally, quaternization of aromatic phosphines (example 21, Table XI) is exemplified for tetraphenylphosphonium bromide.

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Mechanistic Pathways in the Catalytic Carbonylation of Methanol by Rhodium and Iridium Complexes

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I

INTRODUCTION

A. Historical Perspective

Acetic acid has been produced in relatively large quantities for more than 100 years. The changes in the methods used for its production over this period reflect some of the underlying general trends in the chemical industry. It was originally produced via fermentation, as were many other organic chemicals in the early days of the chemical industry. The first major synthetic process for acetic acid was based on the hydrolysis of acetylene to acetaldehyde catalyzed by mercuric ion. This process was the dominant method of production for more than 40 years, until 1955–1960, when two new processes were developed which have dominated the acetic acid markets in the past 20 years. Celanese in the United States and British Petroleum in Europe introduced short-chain paraffin oxida-

tion using manganese or cobalt salts as the catalysts in a free radical process.

Meanwhile, Wacker Chemie developed the palladium-copper-catalyzed oxidative hydration of ethylene to acetaldehyde. In 1965 BASF described a high-pressure process for the carbonylation of methanol to acetic acid using an iodide-promoted cobalt catalyst (1, 2), and then in 1968, Paulik and Roth of Monsanto Company announced the discovery of a low-pressure carbonylation of methanol using an iodide-promoted rhodium or iridium catalyst (3). In 1970 Monsanto started up a large plant based on the rhodium catalyst.

The overall trend in processes indicates a gradual shift away from the high-energy (and usually expensive) intermediates, such as acetylene, toward lower-energy materials, such as paraffins and methanol.

Acetic acid is presently produced on a very large scale. World-wide production in 1977 was approximately 2,500,000 tons. The Monsanto process has now been licensed world-wide, and production from these plants when constructed will amount to more than 1,000,000 tons annually.

B. Methanol Carbonylation Processes

Of the three catalytic systems so far recognized as being capable of giving fast reaction rates for methanol carbonylation—namely, iodide-promoted cobalt, rhodium, and iridium—two are operated commercially on a large scale. The cobalt and rhodium processes manifest some marked differences in the reaction area (4) (see Table I). The lower reactivity of the cobalt system requires high reaction temperatures. Very high partial pressures of carbon monoxide are then required in the cobalt system to

TABLE I
COMPARISON OF COBALT- AND RHODIUM-CATALYZED METHANOL
CARBONYLATION REACTIONS

	Cobalt process	Rhodium process
Metal concentration	$\sim 10^{-1} M$	$\sim 10^{-3} M$
Reaction temperature	$\sim 230^{\circ}\text{C}$	$\sim 180^{\circ}\text{C}$
Reaction pressure	500–700 atm	30–40 atm
Selectivity (on methanol)	90%	> 99%
Hydrogen effect	CH_4 , CH_3CHO , $\text{C}_2\text{H}_5\text{OH}$ formed as by-products	No effect

stabilize the cobalt carbonyl at these high reaction temperatures (5). Another key area of difference between the two processes is sensitivity to hydrogen. While hydrogen is not necessarily present in the reaction feed, impure carbon monoxide streams frequently contain some hydrogen. The rhodium system is insensitive to hydrogen, but the cobalt system produces increased amounts of hydrogenated by-products. This is perhaps not unexpected in view of the report of cobalt catalysis of the methanol plus synthesis gas reaction to give ethanol (6).

II

THE CARBONYLATION OF METHANOL CATALYZED BY RHODIUM COMPLEXES IN SOLUTION

A. Kinetic Studies

Kinetic studies of the rhodium-catalyzed methanol carbonylation reaction (4, 7, 8) show a remarkably simple behavior. The iodide promoter can be charged to the reaction in several different forms without marked differences in the reaction rate being noted. Thus CH_3I , aqueous hydriodic acid, and iodine can all be used as effective promoters. However, alkali metal salts, e.g., NaI , do not function very well. Many different types of rhodium compounds can be charged to the reaction, and at typical reaction temperatures of $150^\circ\text{--}200^\circ\text{C}$, they function as effective catalysts. Furthermore, these different forms of rhodium frequently give almost exactly the same rate of reaction (4). Some French workers have also studied the effect of charging different forms of rhodium to the reaction (8), and while they confirm the Monsanto group's findings that a variety of complexes containing monodentate ligands give very similar reaction rates, they note that the presence of bidentate ligands gives a very slow initial reaction.

The only dependencies noted in the kinetic studies were first-order dependencies on iodide promoter and rhodium concentrations. Thus there was no observed effect of varying methanol concentration, and the partial pressure of carbon monoxide had no effect on the reaction rate. Similarly, the concentration of the products, methyl acetate and acetic acid, has no effect on the reaction rate. Thus we have the unusual situation of a reaction, $\text{CH}_3\text{OH} + \text{CO} \rightarrow \text{CH}_3\text{CO}_2\text{H}$, in which the concentrations of the reactants and product have no kinetic influence.

B. Formation of Active Rhodium Species

Quite different types of rhodium compound can give very similar reaction rates in a system which shows a kinetic dependence on the rhodium catalyst concentration. In particular, rhodium(III) halides and rhodium(I) phosphine complexes give almost identical reaction rates after an initial induction period. Thus, in the case of these two systems, it appears that a common species is being formed.

Spectroscopic investigations have shown that the carbonylation of rhodium(III) halides in alcoholic (9) and aqueous media (10) results in the formation of the dicarbonyldihalorhodate(I) anions, e.g., $\text{RhX}_3 + 3\text{CO} + \text{H}_2\text{O} \rightarrow [\text{Rh}(\text{CO})_2\text{X}_2]^- + \text{CO}_2 + 2\text{H}^+$.

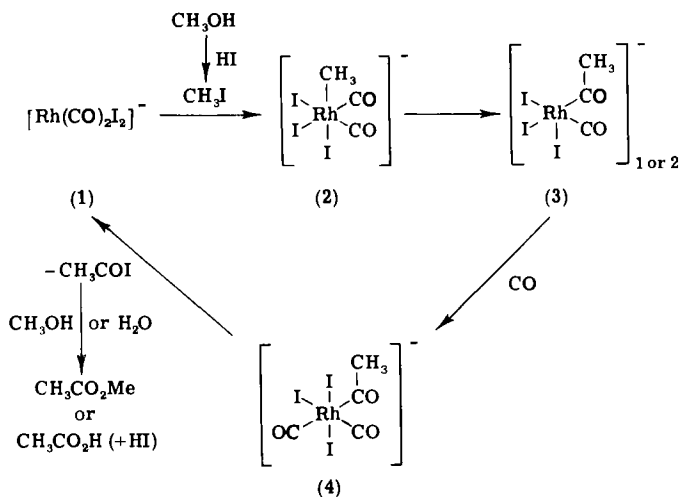
When the rhodium(I) phosphine complexes are charged to the reaction medium as the catalyst precursor, black solids can be isolated by cooling the reaction product in air. This material has a carbonyl stretching frequency ($\sim 2070\text{ cm}^{-1}$) and a proton NMR spectrum with a complex of lines at $\sim 7.8\text{ ppm}$ arising from aromatic protons (relative area 5) and a doublet at 2.93 ppm (relative area 1) which can be assigned as a methyl attached to phosphorus. The phosphorus-proton splitting ($J_{\text{P-H}} \approx 1313\text{ Hz}$) is in the range usually observed for a $\text{CH}_3\text{—P}$ system. It is thus apparent that the phosphines originally attached to the rhodium have become quaternized. Because this leaves the same potential ligands for the rhodium as are present after carbonylation of RhX_3 , it is expected that the same $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ species would form. This was confirmed by conducting a methanol carbonylation reaction using $[\text{Rh}(\text{Ph}_3\text{P})_2(\text{CO})\text{Cl}]$ as the catalyst precursor in a Fischer-Porter glass tube at 10 atm pressure and 100°C . The rhodium complex was not very soluble initially, but after about one hour at reaction temperature, the solids disappeared and a pale yellow reaction solution was observed. A sample was withdrawn from the reactor and the infrared spectrum showed the characteristic spectrum of the $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ ion.

Thus, two quite different forms of rhodium catalyst precursor can give the same rhodium species under the carbonylation reaction conditions.

Pannetier *et al.* (8) observed that the presence of chelating ligands on the rhodium gave a much poorer methanol conversion over a limited reaction period than did reactions using rhodium complexes with monodentate ligands. This may reflect the slower removal and subsequent quaternization of the chelating ligands.

C. Proposed Catalytic Reaction Cycle

Using the $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ ion as an active species, the following catalytic cycle can be proposed.



Scheme 1

The generation of the initial metal-carbon bond in the catalytic cycle by reaction of methyl iodide with a metal carbonyl-containing species has been proposed as a key step in both the cobalt (2) and rhodium (4) catalyzed systems.

The first example of the reaction of methyl iodide with a metal complex to generate a metal-carbon bond was reported by Chatt and Shaw in 1959, when they showed that $[\text{MePt}(\text{PET}_3)_2\text{I}]$ reacted with CH_3I at 100°C to give $[\text{Me}_2\text{Pt}(\text{PET}_3)_2\text{I}_2]$ (11). This type of reaction was subsequently termed "oxidative addition," and its generality has been widely recognized. Chock and Halpern studied the kinetics of the oxidative addition of CH_3I to $[\text{Ir}(\text{Ph}_3\text{P})_2(\text{CO})\text{X}]$ (12) and concluded that the reaction was a simple nucleophilic attack of the metal complex on the alkyl halide with a transition state very much akin to that in the Menshutkin reaction.

The mechanism of the reaction of secondary alkyl halides with low-valent transition metal complexes is considerably more complex, and radical processes have been clearly identified in some cases (13, 14).

Because salts of the $[\text{Rh}(\text{CO})_2\text{X}_2]^-$ ion are not only simple to prepare but rather stable species under ambient conditions, the reaction of $[\text{Rh}(\text{CO})_2\text{X}_2]^-$ ions with methyl iodide can be readily studied. Infrared spectroscopy at room temperature (15) reveals that an acetyl complex of rhodium(III) is the first detectable species after reaction. This species was isolated as its trimethylphenylammonium salt, and the structure of this material has been determined by X-ray crystallography (16). The

rhodium acetyl anion was found to be dimerized through a very weak Rh—I—Rh bridge (see Fig. 1).

This acetyl species (3) reacts very rapidly with carbon monoxide at room temperature to form a species with terminal CO stretching frequencies in the infrared at 2141 (weak) and 2084 (very strong) cm^{-1} and an acetyl frequency at 1708 (strong) cm^{-1} . This species is assigned structure 4, but the stereochemistry is uncertain. Unfortunately, the material is difficult to characterize because of its instability. It decomposes at room temperature, generating $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ and acetyl iodide. This decomposition was studied in several solvents (CHCl_3 , CH_3NO_2 , $\text{C}_6\text{H}_5\text{Cl}$, CH_2Cl_2 , and CH_3OH), and the rate did not show any marked solvent dependence. The corollary of this observation is that oxidative addition of acyl halides to the $[\text{Rh}(\text{CO})_2\text{X}_2]^-$ ions is not a thermodynamically favored reaction; indeed, we have been unable to observe any indication of the formation of rhodium(III) acetyl species by allowing the $[\text{Rh}(\text{CO})_2\text{Br}_2]^-$ and $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ ions to react with very large excesses of acetyl bromide and acetyl chloride, respectively.

This catalytic cycle, generating acetyl iodide from methyl iodide, has been demonstrated by carbonylation of anhydrous methyl iodide at 80°C and CO partial pressure of ~ 3 atm using $[(\text{C}_6\text{H}_5)_4\text{As}][\text{Rh}(\text{CO})_2\text{X}_2]$ as catalysts. After several hours reaction, acetyl iodide can be identified by NMR and infrared techniques. However, under anhydrous conditions some catalyst deactivation occurs, apparently by halogen abstraction from the acetyl iodide, giving rhodium species such as *trans*- $[\text{Rh}(\text{CO})_2\text{I}_4]^-$ and $[\text{Rh}(\text{CO})\text{I}_4]^-$. Such "dehalogenation" reactions are common with d^8 and d^{10} species, particularly in reactions with species containing weak

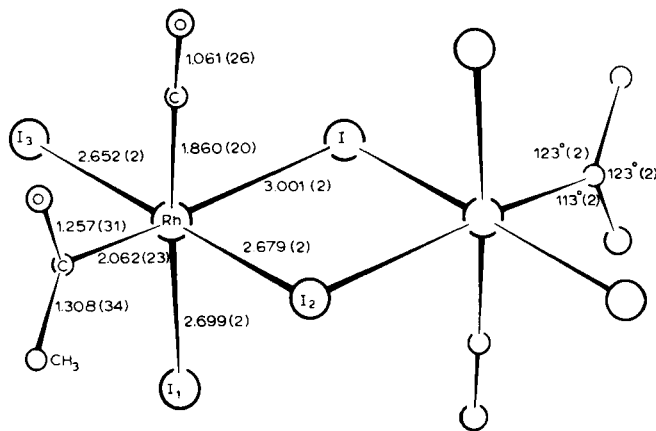


FIG. 1. Structure of the adduct of CH_3I and $[\text{Rh}(\text{CO})_2\text{I}_2]^-$.

carbon-halogen bonds; the C—I bond dissociation energy in CH_3COI is very low (17).

Under the reaction conditions for methanol carbonylation in which hydroxylic solvents are present, acetyl iodide would be solvolyzed very rapidly, giving either acetic acid or methyl acetate together with hydrogen iodide. The hydrogen iodide can rapidly react with more methanol to give methyl iodide to complete the iodide cycle.

The kinetic data have been interpreted (4) as indicating that the rate-determining step in the catalytic cycle is the oxidative addition of methyl iodide to a rhodium(I) species. Hence for systems which can generate the $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ ion, as described earlier, the rate-determining step should be oxidative addition of CH_3I to $[\text{Rh}(\text{CO})_2\text{I}_2]^-$. This was confirmed by a direct infrared spectral examination of a reacting solution using the high-pressure, high-temperature spectrophotometric cell developed by Morris and Tinker of these laboratories (18). A reaction solution was examined at 100°C and 6 atm of carbon monoxide pressure and shown to contain $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ as the principal rhodium species (15).

The $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ ion is clearly an important species in systems derived from several different catalyst precursors; fortuitously, it is a relatively nucleophilic rhodium species. Thus it reacts with methyl iodide at room temperature, whereas the related uncharged species, $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, is unreactive toward methyl iodide at low temperatures. This difference between neutral and charged species is also evidenced markedly in the relative reactivities of $[\text{RhL}_2(\text{CO})\text{X}]$ and $[\text{RhL}(\text{CO})\text{X}_2]^-$ toward methyl iodide, where a difference of five orders of magnitude has been observed (19).

Thus, in the overall catalytic cycle it is observed that the various steps necessary can all occur under mild conditions; therefore, the use of elevated temperatures ($>150^\circ\text{C}$) in the commercial operation is related to increasing the efficiency of the use of the rhodium catalyst by increasing the reaction rate by use of temperature rather than catalyst level.

The observation of extremely facile formation of an acetyl complex and the finding that oxidative addition is the rate-determining step are almost certainly related to the high selectivity observed in the reaction. Thus, the extremely short lifetime of any $\text{CH}_3\text{—Rh}$ species makes it unlikely that it would be reacted off to methane in the presence of hydrogen (and/or metal hydrides).

D. Other Promoters for the Rhodium-Catalyzed Reaction

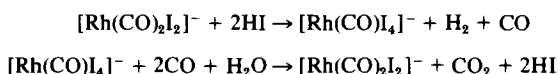
Iodide may be replaced by bromide in the reaction system, but it suffers from the major drawback that the methanol carbonylation rate

becomes very slow. A study of the reaction of methyl bromide with $[\text{Rh}(\text{CO})_2\text{Br}_2]^-$ shows that an acetyl complex analogous to **3** forms but at a rate at least an order of magnitude slower than the analogous reaction with methyl iodide (20).

It has been recently reported that an "organic pseudohalide" can function as a promoter in the methanol carbonylation reaction. Webber *et al.* (21) have shown that pentachlorobenzenethiol will promote the rhodium-catalyzed reaction but at less than 5% of the rate of the iodide system.

E. Potential Side Reactions

The ability of the $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ ion to catalyze the water gas-shift reaction has been recently described (22). The reaction cycle can be broken down into two basic reactions:



Thus, the overall reaction is $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$. Under the reaction conditions of the methanol carbonylation reaction, where hydrogen iodide can be present (*vide supra*), it is apparent that the water gas shift could be a competing reaction. However, very little water gas shift is noted (4, 23). The equilibrium $\text{CH}_3\text{OH} + \text{HI} \rightleftharpoons \text{CH}_3\text{I} + \text{H}_2\text{O}$ clearly is of some importance in determining the extent of competition between CH_3I and HI for reaction with rhodium. The equilibrium constant for this reaction strongly favors methyl iodide; therefore, the water gas-shift reaction is not expected to be a significant competitor, especially in view of the fact that the rate reported for this reaction (22) is not particularly fast compared to the methanol carbonylation reaction.

III

SUPPORTED RHODIUM CARBONYLATION CATALYSTS FOR METHANOL CARBONYLATION

The technique of combining homogeneous catalysis with heterogeneous catalysis by binding or depositing metal complexes onto surfaces

has been widely pursued. Several studies of this type of approach to the methanol carbonylation reaction have appeared (24–26). The Monsanto group of Robinson *et al.* (25) studied the vapor-phase reaction using a catalyst consisting of rhodium carbonyl halides deposited onto activated carbon. The kinetic dependencies observed for the vapor-phase reaction paralleled those observed in the liquid phase, and they concluded that the same mechanism was operative.

A different type of heterogeneous catalyst was used by Jarrell and Gates (26). They exchanged $[\text{Rh}(\text{Ph}_3\text{P})_2(\text{CO})\text{Cl}]$ onto the surface of a thin film of phosphinated polystyrene, thus obtaining a rhodium complex attached to the surface via a rhodium–phosphine link. This catalyst was studied by transmission infrared spectroscopy while reacting at 100°C. The catalyst was observed to deactivate and gradually form a species with a CO stretching frequency at 2063 cm^{-1} . Jarrell and Gates suggested that this inactive form was the iodine adduct of $[\text{Rh}(\text{polymer phosphine})(\text{Ph}_3\text{P})(\text{CO})\text{Cl}]$. However, a follow-up study of this system by Schmidt and Forster (27) suggests a different interpretation of the results. Schmidt and Forster used ESCA to show that the phosphorus binding energy of used catalyst was identical with that observed by quaternization of phosphinated polymer with CH_3I , i.e., that during the reaction the coordinated phosphine groups are removed from the metal and quaternized. The used catalysts were then subjected to several chemical transformations as an aid to deducing the nature of the surface species. It was found that treatment of the used catalysts displaying carbonyl stretching bands at 1992, 2065, and 2087 cm^{-1} with a solution of tetrapropylammonium iodide in nitromethane gave a solution containing $[\text{Rh}(\text{CO})_2\text{I}_2]^-$, $[\text{Rh}(\text{CO})\text{I}_5]^{2-}$, and *trans*- $[\text{Rh}(\text{CO})_2\text{I}_4]^-$. Treatment of the used catalyst with solutions containing Ph_3P removed all of the carbonyl bands from the surface and gave $[\text{Rh}(\text{Ph}_3\text{P})_2(\text{CO})\text{I}]$ and $[\text{Rh}(\text{Ph}_3\text{P})_2(\text{CO})_2\text{I}]$ in solution. Subsequent treatment of these “extracted” catalysts with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ gave a polymer showing the CO stretching bands of $[\text{Rh}(\text{CO})_2\text{I}_2]^-$. These experiments all point to the rhodium form on the catalyst surface being anionic and associated with quaternized phosphine cations.

Both the approaches discussed above are addressed to the desire for immobilization of the metal species, while the corrosive and volatile promoter must still be trapped and recycled. Recently, Webber *et al.* (28) have attempted to achieve immobilization of both the metal species and the promoter by attaching rhodium to a polymer functionalized with chlorinated thiophenol groups. This imaginative approach is presently plagued by both low reactivity and rhodium loss from the polymer surface.

IV

IRIDIUM-CATALYZED METHANOL CARBONYLATION

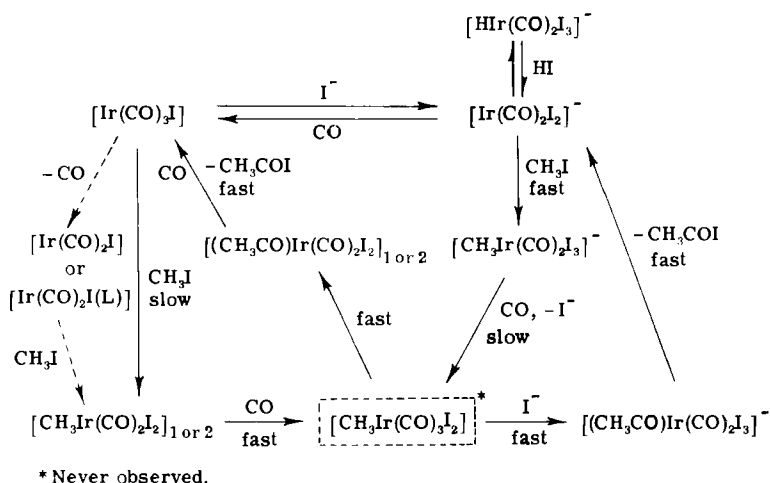
Iridium is also an excellent homogeneous catalyst for the carbonylation of methanol under relatively mild reaction conditions (3). Two reports of mechanistic investigations have appeared (29), (30), and further studies will be reported (31). It is clear that the iridium system is considerably more complicated than the rhodium system. Unfortunately, there is little agreement among the various investigations with respect to the kinetic effects of reaction parameter variations. There are apparently complex interactions among solvent, water, iodide form, and carbon monoxide pressure, and this complicates interpretation. Some general kinetic observations from the Monsanto group study can be made: (a) The reaction rate is strongly dependent on water concentration, with a decrease in rate being observed at higher water levels; (b) in reaction media containing appreciable concentrations of iodide ion, the reaction rate increases with increasing carbon monoxide pressure; (c) the reaction rate is not first order with respect to methyl iodide concentration as in the rhodium system, but shows an optimum level; and (d) at low iodide levels using methyl acetate as the substrate with low levels of water present, the reaction rate is inversely dependent on carbon monoxide pressure.

Spectroscopic investigations have been carried out by the Monsanto group. Most observations were made on samples withdrawn from the reactor and observed under ambient conditions, but many *in situ* spectroscopic measurements were also made. The conclusion reached from these studies was that there were at least two catalytic cycles with the iodide ion concentration being the principal factor controlling the choice of cycle. Thus, it is observed that when reactions are conducted in methyl acetate with low levels of water in order to maintain a low level of methanol and with relatively low levels of methyl iodide (e.g., $\text{CH}_3\text{I}:\text{Ir}$ of 10:1), the predominant iridium species observed spectroscopically is $[\text{Ir}(\text{CO})_3\text{I}]$. The reaction rate is slowed by increasing carbon monoxide pressure under these conditions. However, as the concentration of either water, methanol, methyl iodide, or simply iodide ion is substantially increased, a change in the predominant iridium form to one of several iridium(III) species is observed. When iodide ion alone is increased, $[\text{CH}_3\text{Ir}(\text{CO})_2\text{I}_3]^-$ is the predominant form observed and the reaction rate is increased by increasing CO pressure. If the methyl iodide and water levels are increased, the predominant form of iridium becomes $[\text{HIr}(\text{CO})_2\text{I}_3]^-$.

The chemistry of $[\text{Ir}(\text{CO})_3\text{I}]$, $[\text{Ir}(\text{CO})_2\text{I}_2]^-$, and $[\text{CH}_3\text{Ir}(\text{CO})_2\text{I}_3]^-$ has been explored independent of the carbonylation reaction. Some of the perti-

nent findings are: (a) $[\text{Ir}(\text{CO})_2\text{I}_2]^-$ is much more reactive toward methyl iodide than $[\text{Ir}(\text{CO})_3\text{I}]$; (b) $[\text{Ir}(\text{CO})_3\text{I}]$ reacts with methyl iodide at room temperature and pressure to give predominantly $[\text{CH}_3\text{Ir}(\text{CO})_2\text{I}_2]_2$ with some $[(\text{CH}_3\text{CO})\text{Ir}(\text{CO})_2\text{I}_2]$, i.e., dicarbonyl species, but under 5 atm of carbon monoxide at 100°C in a dry solvent it generates acetyl iodide and $[(\text{CH}_3\text{CO})\text{Ir}(\text{CO})_2\text{I}_2]_{1 \text{ or } 2}$; (c) $[\text{Ir}(\text{CO})_3\text{I}]$ reacts with oxygen donors to give species of the type $[\text{Ir}(\text{CO})_2(\text{L})]$ which are more reactive toward methyl iodide; (d) the oxidation addition of methyl iodide to $[\text{Ir}(\text{CO})_2\text{I}_2]^-$ gives $[\text{CH}_3\text{Ir}(\text{CO})_2\text{I}_3]^-$, unlike the analogous rhodium system which gives an acyl species; (e) the $[\text{CH}_3\text{Ir}(\text{CO})_2\text{I}_3]^-$ ion shows no tendency to isomerize to an acyl species up to 150°C , but can be converted to $[(\text{CH}_3\text{CO})\text{Ir}(\text{CO})_2\text{I}_3]^-$ together with $[\text{Ir}(\text{CO})_2\text{I}_2]^-$ and CH_3COI by treatment with 5 atm of carbon monoxide at 90°C for several hours; and (f) the conversion of $[\text{CH}_3\text{Ir}(\text{CO})_2\text{I}_3]^-$ to an acyl species by treatment with carbon monoxide is inhibited by excess iodide ion.

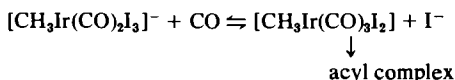
The kinetic dependencies together with the chemical observations above lead to the following scheme for the catalytic reaction:



Scheme 2. Catalytic cycles for the iridium-catalyzed carbonylation of methanol.

The ionic cycle is important under reaction conditions where iodide ion can exist, e.g., higher water levels ($\text{CH}_3\text{OH} + \text{HI} \rightleftharpoons \text{CH}_3\text{I} + \text{H}_2\text{O}$) or with salt additives. However, while higher ionic iodide levels give an iridium species capable of very rapid reaction with methyl iodide, they also serve to inhibit the formation of an acyl species. The relatively slow conversion of $[\text{CH}_3\text{Ir}(\text{CO})_2\text{I}_3]^-$ to an acyl species is almost certainly not

caused by a slow ligand exchange on this octahedral d^6 species, for the three strong trans-influencing ligands make the halides on $[\text{CH}_3\text{Ir}(\text{CO}_2\text{I}_3)]^-$ relatively labile, and halide exchange is complete within minutes at room temperature (33). Rather, the slowness of the transformation appears to be due to the very low equilibrium concentration of the tricarbonyl species presumably necessary to induce methyl migration, i.e.,



This would not be too surprising, for tricarbonyl derivatives of trivalent metals are rare and expected to be very unstable. The positive effect of CO pressure on the reaction rate is thus readily explicable when this species is the predominant form observed. Mizoroki *et al.* (30) claim that the predominant iridium form in their reaction media is an acetyl species, because they isolate $[\text{CH}_3\text{CO}]\text{Ir}(\text{CO})\text{I}_2(\text{Ph}_3\text{P})_2$ by treatment of a reaction solution with triphenylphosphine. However, we have found that $[\text{CH}_3\text{Ir}(\text{CO})_2\text{I}_3]^-$ reacts with Ph_3P to give $[(\text{CH}_3\text{CO})\text{Ir}(\text{CO})\text{I}_2(\text{Ph}_3\text{P})_2]$, and thus this experiment does not readily distinguish between the alkyl- and acyl-iridium species in solution.

A further complication is evident in the spectroscopic studies of the reacting iridium solutions, namely, a competing catalytic water gas shift reaction involving hydrido-iridium(III) species. Choice of reaction conditions determines the proportion of the iridium occupied in this catalytic cycle.

The rate of the methanol carbonylation reaction in the presence of iridium catalysts is very similar to that observed in the presence of rhodium catalysts under comparable conditions (29). This is perhaps initially surprising in view of the well-recognized greater nucleophilicity of iridium(I) complexes as compared to their rhodium(I) analogues. It can be seen from the above studies that the difference in the chemistry of the metals at the trivalent stage of the catalytic cycle serves to produce faster rates of alkyl migration with the rhodium system; thus, overall the two metal catalysts give comparable rates.

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Catalytic Codimerization of Ethylene and Butadiene¹

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I

INTRODUCTION

The catalytic transformation of olefins by transition metal complexes has received a great deal of attention during the past two decades. These catalytic reactions are important, especially industrially, because they represent some of the most economical ways to synthesize olefinic monomers or polymers. The more common types of these transformation reactions are: (a) dimerization or polymerization of α -olefins; (b) dimerization, oligomerization, cyclooligomerization, or polymerization of con-

¹Contribution No. 429.

jugated dienes; and (c) codimerization or cooligomerization of α -olefins and conjugated dienes.

The codimerization reaction we will discuss in this chapter belongs to the last type. The reaction and the reactants involved will be the simplest of them all, i.e., a 1:1 codimerization of ethylene and butadiene to form C_6 dienes.

Catalysts for this codimerization reaction can be derived from practically all the Group VIII transition metal compounds. Their catalytic properties, such as rate, efficiency, yield, selectivity, and stereoselectivity, vary from poor to amazingly good. Some better-known catalyst systems and their product distributions are listed in Table I. As one can see, the major codimerization product under the given condition is the linear 1:1 addition product, 1,4-hexadiene. The formation of this diene and its related C_6 products will become the center of our discussions. The catalyst systems that have been investigated rather extensively are derived from Rh, Ni, Co, and Fe. We shall cover these systems in some detail. A lesser-known catalyst system based on Pd will also be briefly discussed.

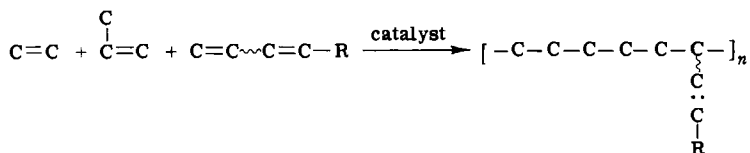
Before we continue I would like to mention briefly the practical reasons leading to the study of this codimerization reaction.

In the 1950's it was discovered that synthetic rubber with outstanding properties can be obtained by copolymerizing ethylene and propylene using Ziegler's type coordination catalyst systems. However, these rubbers contained only saturated hydrocarbon backbones which were unable to undergo the type of cross-linking or vulcanization needed to achieve high tensile strength. In order to create cross-linking sites, some unsaturation must be put into the polymer chain. This can be achieved by introducing into the polymerization system a diene containing both ter-

TABLE I
TYPICAL ISOMER DISTRIBUTIONS IN 1:1 CODIMERIZATION OF ETHYLENE AND BUTADIENE BY VARIOUS TRANSITION METAL CATALYSTS

Catalyst	<i>trans</i> -1,4-Hexadiene	<i>cis</i> -1,4-Hexadiene	3-Methyl 1,4-pentadiene	2,4-Hexadiene
RhCl ₃ /C ₂ H ₅ OH	80	10	<1	10
[Bu ₃ P] ₂ NiCl ₂ + R ₂ AlCl	55	20	15	10
[Ph ₂ PCH ₂ —CH ₂ PPh ₂] ₂ CoCl ₂ + R ₂ AlCl	—	95–100	—	Trace
[Ph ₂ PCH ₂ CH ₂ PPh ₂] ₂ FeCl ₂ + R ₂ AlCl	—	95–100	—	Trace
PdCl ₂ /R ₃ P + R ₂ AlCl	77	—	—	Trace

terminal unsaturation that can participate in the polymerization reaction and internal unsaturation that will be inert to the polymerization and thus remain pendent to the polymer chain:



The pendent unsaturation provides a site for vulcanization or cross-linking, e.g., by sulfur derivative.

The simplest diene that satisfies this requirement is 1,4-hexadiene, and indeed it has been adopted as the cure site monomer in commercial ethylene-propylene-diene rubber. Because 1,4-hexadiene exists in both trans and cis configurations, significant amounts of work have been devoted to find ways to control the selectivity of the catalysts for one of the isomers over the other.

II

THE RHODIUM CATALYST SYSTEM

A. Background

1:1 Codimerization of ethylene and butadiene was first carried out by Alderson (1, 2) starting with rhodium trichloride trihydrate, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, as catalyst. He reported that the major product was 1,4-hexadiene with a trans/cis ratio which favored the trans isomer. An example of the reaction involves heating 3.2 moles of C_4H_6 , 2.7 moles of C_2H_4 , 0.2 g of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, and 1 ml of ethanol in a 400 ml silver-lined autoclave. After 16 hours at 50°C , the conversion of butadiene is 54%. The products consisted of 91% C_6 diene (80% 1,4-diene, 20% conjugate diene), 2% butene, 3% C_8 dienes, and 4% higher olefins. Alderson determined that the major 1:1 adduct, 1,4-hexadiene, was the result of addition of ethylene to butadiene; that the conjugated diene (2,4-hexadiene) arose as a result of double bond isomerization of the 1,4-diene; and that the higher olefins arose from interaction of the conjugated dienes with excess ethylenes. Furthermore, the amounts of these by-products increased with increasing temperature and butadiene conversion. According to Alderson, the addition reaction among unlike molecules, i.e., ethylene and butadiene, was 50 times more likely than the reactions among like molecules. The selectivity was rather surprising, as the same catalyst dimer-

izes ethylene at about the same rate under the same reaction condition (3).

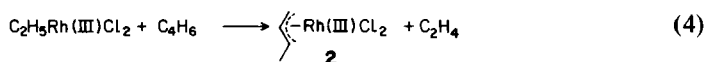
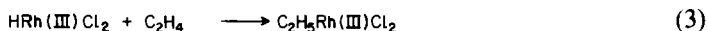
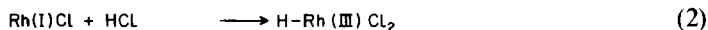
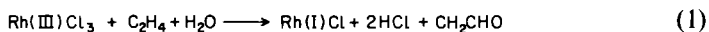
This preferential formation of 1:1 adduct to form 1,4-hexadiene in a mixture of ethylene and butadiene was further studied by Cramer (4). He concluded that the results appeared to be the consequence of thermodynamic control reactions through a relatively stable π -crotyl Rh complex.

B. Catalytic Mechanism of Additions of Ethylene to Butadiene

The most general and comprehensive reaction mechanism of the 1:1 codimerization has been reported by Cramer (4). The results were based on reaction properties measured in an alcoholic medium under relatively mild conditions.

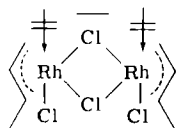
1. Catalyst Activation and Nature of the Active Species

The starting catalyst complex, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, as described by Alderson is not the active form of the catalyst. It must undergo a series of transformations before the actual functioning species is generated. This activation reaction under the dimerization condition was described by Cramer (4) and is represented in Scheme 1. It begins with the reduction of the Rh^{III} chloride to a Rh^{I} complex in the presence of H_2O and C_2H_4 with generation of HCl and acetaldehyde [Eq. (1) in Scheme 1]. Conversion of the Rh^{I} species back into a Rh^{III} hydride by oxidative addition reaction involves HCl [Eq. (2)]. The hydride then reacts with coordinated olefin, most likely ethylene, to give a Rh^{III} alkyl [Eq. (3)]. In the presence of excess butadiene, ethylene may be replaced by butadiene to give a π -crotyl rhodium^{III} complex 2 [Eq. (4)] which, as we shall see in Section II,B,2, becomes the key intermediate complex in the catalytic cycle.



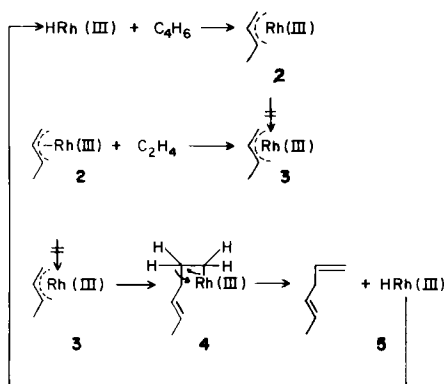
SCHEME 1. Rh catalyst activation. The equations shown here are based on net reactions only.

Cramer has isolated this π -crotyl complex in its stable dimeric form (1) by interacting butadiene with an ethyl-Rh^{III} chloride (4):



(1)

As a result of the above activation reaction, an induction period is thus noticeable, especially at lower temperature if one uses RhCl·3H₂O as the starting catalyst. However, if one starts with a Rh^I complex, e.g., (C₂H₄)₂Rh^ICl (5) or (C₂H₄)₂Rh^I(acac) (6) in the presence of HCl and alcohol, this induction period is eliminated because the Rh^I will react immediately with HCl, leading to the formation of the active species. The catalytic cycle starting from the π -crotyl species 2 is depicted in Scheme 2. This involves coordination of the π -crotyl species with ethylene to form complex 3 and insertion of C₂H₄ into the crotyl-Rh bond resulting in the formation of the hexyl complex 4. A β -elimination reaction from this hexyl complex generates rhodium hydride and produces 1,4-hexadiene. The hydride then reacts with another molecule of butadiene to form the crotyl complex and completes the catalytic cycle. The net result of the addition reaction corresponds to a 1,4-addition of a hydrogen and a vinyl group to the conjugated diene system. This 1,4-addition sequence appeared to be general for all metal-catalyzed 1,3-diene addition reactions where the reactions are initiated by the addition



SCHEME 2. Catalytic cycle for Rh catalyst for 1:1 codimerization of ethylene and butadiene to form 1,4-hexadiene.

of metal hydrides. Throughout the above reaction sequences, Rh remains in the trivalent state. This is different from the Rh-catalyzed ethylene dimerization reaction (3) where the valence of Rh oscillates between one and three.

2. Reaction Kinetics

The rate equation for the dimerization of ethylene (3) can be used to describe the codimerization in the presence of large excesses of butadiene. The rate of the addition reaction as measured by the disappearance of ethylene is represented in Eq. (5). It is first order in ethylene, proton, chloride, and rhodium.

$$\frac{-d[\text{C}_2\text{H}_4]}{dt} = k[\text{C}_2\text{H}_4][\text{H}^+][\text{Cl}^-][\text{Rh}] \quad (5)$$

The rate also varies with butadiene concentration. However, the order of the rate dependence on butadiene concentration is temperature-dependent, i.e., a fractional order (0.34) at 30°C and first-order at 50°C (Tables II and III). Cramer's (4, 7) explanation for this temperature effect on the kinetics is that, at 50°C, the insertion reaction to form 4 from 3, although still slow, is no longer rate-determining. Rather, the rate-determining step is the conversion of the hexyl species in 4 into 1,4-hexadiene or the release of hexadiene from the catalyst complex. This interaction involves a hydride transfer from the hexyl ligand to a coordinated butadiene. This transfer should be fast, as indicated by some earlier studies of Rh-catalyzed olefin isomerization reactions (8). The slow release of the hexadiene is therefore attributed to the low concentration of butadiene. Thus, Scheme 2 can be expanded to include complex 6, as shown in Scheme 3. The rate of release of hexadiene depends on the concentra-

TABLE II
EFFECT OF BUTADIENE CONCENTRATION ON THE RATE OF
ADDITION OF ETHYLENE TO BUTADIENE AT 50°C^a

$[\text{C}_4\text{H}_6]$ (arbitrary units)	$\frac{d \ln (P - P_\infty)}{dt} \times 10^5$ (sec ⁻¹)	$\frac{\text{slope}}{[\text{C}_4\text{H}_6]} \times 10^5$
1	5.48, 5.18	4.48, 5.18
2	10.3, 10.2	5.15, 5.10
3	15.7, 15.9	5.23, 5.30

^a Data from Cramer (4).

TABLE III
EFFECT OF BUTADIENE CONCENTRATION ON THE RATE OF
ADDITION OF ETHYLENE TO BUTADIENE AT 30°C^a

$[C_4H_6]$ (arbitrary units)	$\frac{d \ln (P - P_\infty)}{dt} \times 10^5$ (sec ⁻¹)	$\frac{\text{slope}}{0.34[C_4H_6]} \times 10^5$
1	4.56, 4.03	4.56, 4.03
2	5.62, 5.83	4.42, 4.56
4	7.14, 6.50	4.42, 4.03
8	9.28, 8.82	4.45, 4.31

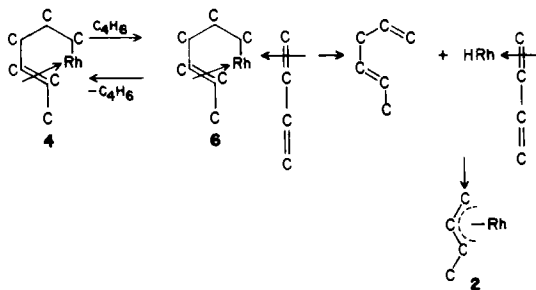
^a Data from Cramer (4).

tion of complex **6**, which in turn depends on the concentration of butadiene.

In practice, butadiene is present in large excess, so that the insertion reaction (**3** → **4**, see Scheme 2), which depends only on the concentration of ethylene, becomes the rate-determining step.

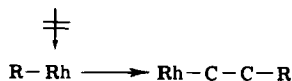
C. Basis for Selectivity toward Formation of C₆ Diene

In the codimerization reaction, both reactants are present in large excess compared to the catalyst concentration. The selectivity toward a 1:1 codimerization to form 1,4-hexadiene, instead of a random oligomerization, represents a rather unique reaction, especially in view of the fact that the same catalyst also dimerizes ethylene to butene (**3**) at about the same rate as the codimerization. The explanation forwarded by Cramer (4, 7) is based on the overwhelmingly favored stability of the π -



SCHEME 3. Steps involved in release of 1,4-hexadiene from Rh catalyst.

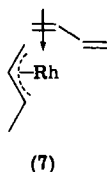
crotyl complex compared to other possible alkyl-Rh complexes that might be formed in the reaction system. The insertion reaction



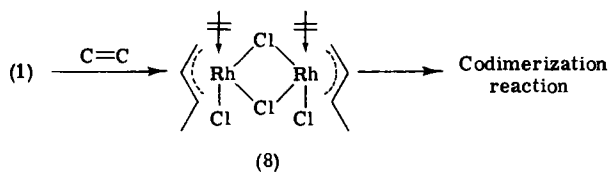
is expected to be slow regardless of the R group on the rhodium atom (2). Thus, the composition of the products is determined by the relative concentration of the type of intermediate complex:



In this codimerization reaction, the predominant complex is 3, which should lead to the ethylene-butadiene codimerization product. If the ethylene in complex 3 is displaced by butadiene to form 7 before the insertion reaction takes place, then a C_8 or higher olefin could be formed



instead of the C_8 product. However, this butadiene dimerization reaction has been shown by Alderson (1) to be very slow under the codimerization condition in the absence of the ethylene. Moreover, Cramer was able to demonstrate that the coordinated butadiene in 1 could be readily displaced by ethylene (Fig. 1) under relatively mild conditions:



Thus it becomes unlikely that 7 can exist long enough to allow extensive dimerization or oligomerization of butadiene. It has also been speculated (7, 9) that the presence of coordinated chlorides on the Rh complex prevents the occurrence of butadiene polymerization reaction.

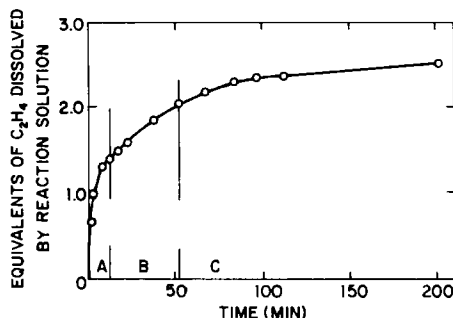
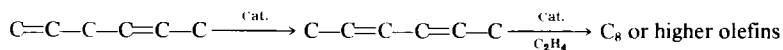


FIG. 1. Absorption of ethylene by a suspension of 0.35 g of $(\pi\text{-C}_4\text{H}_7)_2\text{Rh}_2\text{Cl}_4(\text{C}_4\text{H}_6)$ in 15 ml of 1.2 *M* methanolic HCl. Data from Cramer (4).

D. Isomerization and By-Product Formation

1. Isomerization Reaction

1,4-Hexadiene is the immediate product found in the codimerization reaction described above in a mixture of ethylene and butadiene. However, the reaction will not stop at this stage unless there is an overwhelming excess of butadiene and an adequate amount of ethylene present. As the conversion of butadiene increases, some catalyst begins to isomerize 1,4-hexadiene to 2,4-hexadiene:



The conjugated diene (including the trans-trans, trans-cis, and cis-cis isomers) can further add ethylene to form C₈ olefins or even higher olefins (1). The mechanism of isomerization is proposed to be analogous to butene isomerization reactions (4, 8), i.e., 1-butene to 2-butene, which involves hydrogen shifts via the metal hydride mechanism. A plot of the rate of formation of 2,4-hexadiene vs. butadiene conversion is shown in Fig. 2.

2. 1,2-Addition Product

1,4-Hexadiene which is formed by 1,4-addition of hydrogen and a vinyl group to butadiene, is the predominant product in the codimerization reaction. However, there is always a small amount (1–3%) of 3-methyl-

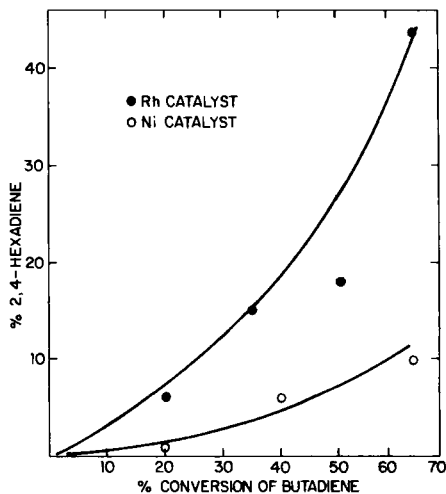
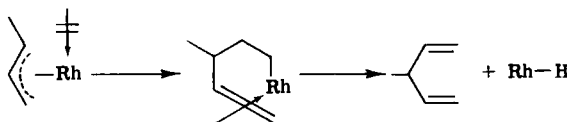


FIG. 2. Production of 2,4-hexadiene vs. C_4H_6 conversion.

1,4-pentadiene formed as a result of a 1,2-addition to butadiene during the following reaction:



The quantity of this by-product apparently is not affected by butadiene conversion (1) or other changes in reaction conditions.

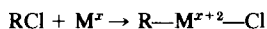
E. Chemistry of Catalyst Decay and Reactivation

The Rh-based dimerization catalyst described above cannot maintain its activity indefinitely. After prolonged reaction (several hours) or after removal of the products and monomers from the reaction mixture, it becomes deactivated or decays to an inactive species. Because Rh metal is very expensive, it becomes desirable to seek a way to rejuvenate the "dead" catalyst. The generally recognized mode of decay is the degeneration of the active Rh^{III} to an inactive Rh^I complex (10-12), e.g., $R-Rh^{III}Cl \rightarrow RCl + Rh^I$.

Verbanc (11) found that, after removal of the products and monomers from the catalyst mixture, the remaining Rh catalyst residual is inactive

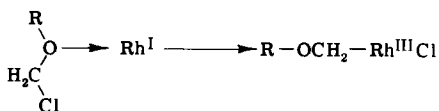
when the reactor is recharged with the monomers, i.e., butadiene and ethylene. However, he found that if enough HCl is added to the reaction mixture the catalyst activity is almost totally recovered. In Cramer's kinetics described earlier, the rate dependence on the concentration of H^+ and Cl^- in the reaction mixture could be linked at least in part to the reactivation of the decayed species Rh^I back to the active Rh^{III} state.

Restoration of the decayed species to its active valence is thus the key to reactivating the catalyst. It has been known that organic halides with activated C—Cl bonds can add to lower-valent transition metals and convert them to their higher oxidation states by oxidative addition (12–16):



Taking advantage of this fact, Su and Collette (10, 16a) studied the possibility of using organic halides as *in situ* activators to continuously reactivate the Rh catalyst in the 1,4-hexadiene synthesis. It was found that many RCl's did activate Rh catalyst. The effectiveness depends on the structure of the organic halides. In general, allylic chlorides, benzylic chlorides, α -chloroethers, and chlorides with C—Cl bonds adjacent to a carbonyl group, such as hexachloroacetone, are effective activators. Aliphatic and aromatic chlorides except CCl_4 ² are not effective activators. Certain vinyl chlorides, such as $(CH_3)_2C=CH-Cl$, are moderately effective, while vinyl chloride,³ vinylidene dichloride, and 1,2-dichloroethylene are not.

The effectiveness of an organic chloride in activating the catalyst appears to be related to the lability of the C—Cl bonds and probably also to their coordinating ability with the Rh. For example, CH_3O-CH_2Cl and $CH_2=CH-CH_2Cl$ were found to be extremely effective activators; presumably, the presence of the ether or the allylic donor sites adds to the ease of the oxidative addition reaction:



² CCl_4 is a slow activator when used in very large quantity.

³ Addition of vinyl chloride to a reaction mixture containing some mildly basic electron donor such as dimethylacetamide (DMAC) converts the Rh^I complex to an active catalyst. It was found (10) that this was not due to direct oxidation of Rh^I by vinyl chloride, but rather to the oxidation of Rh^I by HCl generated by the interaction between vinyl chloride and dimethylacetamide catalyzed by Rh^I :

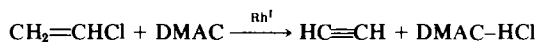


TABLE IV
RELATIVE CATALYST ACTIVITY OF $[(C_2H_4)_2Rh^I Cl]_2$ COMPLEX ACTIVATED FROM
VARIOUS ORGANIC CHLORIDES^a

	Hexadiene produced (g) at			
	15 min	30 min	60 min	120 min
CH_3O-CH_2Cl	25	60	110	
Crotyl-Cl	15	30	60	
$PhCCl_3$	6	15	30	60
$PhCCl_3$		21	50	
$Cl_3CCOCCl_3$	23	6	20	50
Ph_3CCl	Traces	4	14	70
CCl_4^b	Traces			30
1-Chloro-2-methylpropene	Traces	2	6	15
Chloroprene	Traces	Traces	3	10

^a Reaction conditions: 70°C, 9.5 atm ethylene pressure, 180 g C_4H_6 , 20 ml DMAC, $\frac{1}{2}$ mmole $[(C_2H_4)_2RhCl]_2$ complex, and 100 mmoles organic chlorides.

^b CCl_4 was used as solvent in the reaction.

Table IV and Fig. 3 provide a comparison of the effectiveness of some of the activators. These comparisons are based on the amounts of C_6 dienes produced within a given period of time after the addition of the organic chloride to a totally inactive Rh^I complex. As can be seen from Fig. 3, the very best activator triggers the catalytic reaction with almost unnoticeable induction period, while a substantial induction period is apparent with the least efficient activator.

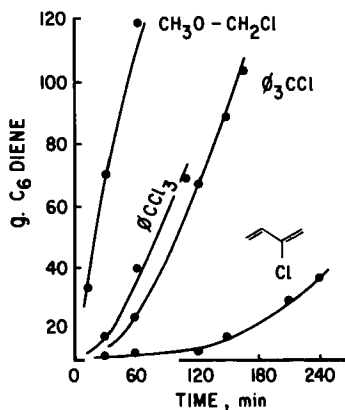


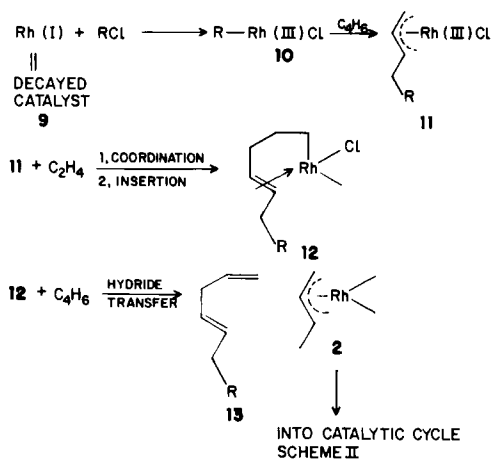
FIG. 3. Relative activity of Rh catalyst activated by RCl. Initial catalyst composition = $\frac{1}{2}$ mM $(Et_2RhCl)_2$ + 100 mM RCl.

Similar to Schemes 1 and 2, the series of reactions leading to the generation of the active species can be represented in Scheme 4.

Following the reactions in Scheme 4, the olefin **13** would have to be generated before the formation of the π -crotyl species **2**. Because the amount of the catalyst present is usually small as compared to the amount of product formed (1000 moles of product/mole catalyst), the quantity of **13** produced will not be significant and should be readily separable from the desired product. In the special case when crotyl chloride is used as the activator, hexadiene can be produced during the very first cycle of reaction, i.e., **13** = 1,4-hexadiene. Among the organic halides, the chloride derivatives are the most effective activators. Bromides are somewhat effective, while fluorides and iodide are rather ineffective (17).

The practical aspect of these reactivation reactions is that, if the reaction mixture contains an excess of a nonvolatile or high-boiling activator, the catalyst can be used repeatedly or recycled after removal of the product and excess monomers. Table V and Fig. 4 summarize an experiment in which a catalyst mixture containing a sufficient excess of a high-boiling organic chloride, PhCCl_3 , was used repeatedly (i.e., recycled after removal of product, solvent, and excess monomers) with no significant loss in catalyst activity. In the absence of the organic chloride, the catalyst lost 80–90% of its activity after being used once under the same conditions.

The use of organic halide to reactivate a decayed catalyst has been known for other catalytic processes involving transition metal catalysts, especially in olefin polymerization reactions (18–21).



SCHEME 4. Catalyst activation by organic chlorides.

TABLE V
RECYCLIZATION OF CATALYST MIXTURE^a AND CATALYST REACTIVATION

	Butadiene conversion ^b (%)	Total C ₆ dienes ^b (g)	1,4-Hexadiene (g)	2,4-Hexadiene (g)	3-Methyl-1,4-pentadiene
Initial run	66	160	117	31	1
First recycle ^c	7	19	19	Traces	Traces
Second recycle ^d	50	123	102	20	1
Third recycle	46	114	95	18	1
Fourth recycle	44	109	91	17	1
Fifth recycle	46	114	95	18	1

^a Starting catalyst: (C₄H₇)₂Rh₂Cl₄C₄H₆ (1 mmole); reaction time, 2 hours.

^b Initial butadiene 180 g. Butadiene conversion = wt. butadiene used/wt. initial butadiene. The yield of C₆ diene with respect to butadiene converted decreased with increasing conversion.

^c No activator added.

^d Addition of 200 mmoles PhCCl₃.

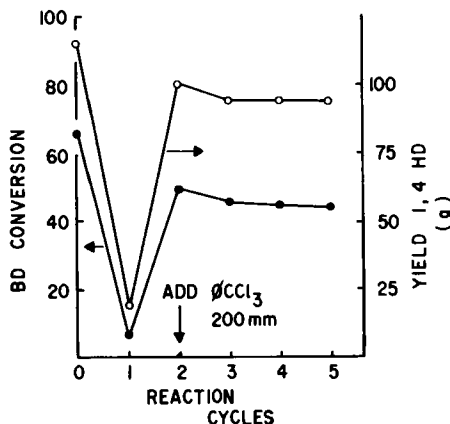
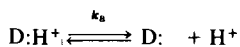
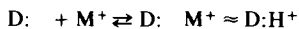


FIG. 4. Effect of PhCCl_3 on activity of Rh catalyst.

F. Effect of Solvating Ligands on the Reaction Properties

The Rh catalyst system described here is highly sensitive to the coordination or solvation effect of electron donor ligands that might be present in the reaction system. The mechanistic studies in Section II,B were based on studies in alcoholic medium, and this imposes a constant influence on the catalytic property as a result of coordination or solvation to the catalyst of the alcohol molecules. In order to study the effect of other coordinating ligands on the catalytic property, Su and Collette (22–24) reexamined the dimerization reaction in a nonpolar medium (toluene) containing a controlled quantity of various donor ligands. The effect of these donor ligands on the catalyst activity to produce the 1:1 addition product 1,4-hexadiene, as well as their influence on the stereoselectivity between the trans and cis isomers of this diene, was then examined. The reaction conditions were designed so that the catalytic synthesis of 1,4-hexadiene could be examined with minimum interference from by-product formations. This was achieved by having a large excess of butadiene in the reaction mixture and carrying the reactions to relatively low (15–20%) conversions. To avoid an induction period, the crotyl-Rh complex 1 was used as catalyst instead of the usual $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$.

In order to compare donor strengths of different donor ligands, Su and Collette found it convenient simply to use the $\text{p}K_a$ values (23) of the onium salts of various donors. This is based on the assumption that the complexation of Rh with a donor is analogous to an acid–base interaction:



The basicity of the donors, which is proportional to the pK_a values, becomes a measure of the relative donor strength. Thus, diglyme ($pK_a \sim 4$) is a weak donor, while Bu_3PO ($pK_a \sim 0$) is a strong donor.

1. Effect of Donor Ligands on the Rate of Reaction

It was found that, in a nonpolar medium, the crotyl rhodium complex 1 is relatively inactive as a codimerization catalyst. However, it becomes very active in the presence of a small amount of donors such as alcohol. The activity generally increases linearly with the amount of the added donors and then depends on the strength of the donors, either leveling off or decreasing with further increases in the donor concentration. Strong donors improve the activity at lower concentration but inhibit the reaction at higher concentration. Some representative donors and their rate enhancement efficiency are shown in Table VI. The relationships between the concentrations of various donors and the reaction rates are summarized in Figure 5. The rate enhancement efficiency (expressed as relative reactivity) of a donor was measured based on the maximum rate attainable by addition of a suitable quantity of the donor to the reaction mixture, i.e., the maximum in the activity curve of Fig. 5. The results in Table VI show that those donors with pK_a values (25) between -5 and

TABLE VI
RELATIVE EFFECT OF VARIOUS DONORS ON CATALYST ACTIVITY

Donor	pK_a^a	Optimum donor/ Rh	Relative reactivity ^b
None	—	—	1
Bu_3PO	0	2	1.3
$CH_3C \equiv O - N(CH_3)_2$	-0.5	300	5
H_2O^c	-1.9	300	8
Alcohols	-2 to -1	~ 500	6-8
THF	-2.1	~ 500	5
Diglyme	~ -4	3000-4000	6
Ethyl acetate	-6.5	4000	6.5
Phenol ^d	-6.8	ND ^e	1 (Donor/Rh=200)
Acetone	-7	4000	6
			3 (Donor/Rh=200)
Pyridine	>5.3	—	0

^a Arnett (25).

^b Based on amount of 1,4-hexadienes formed in first 15 minutes reaction time.

^c Reaction carried out in diglyme.

^d Phenol is anomalous; see discussion.

^e Not determined.

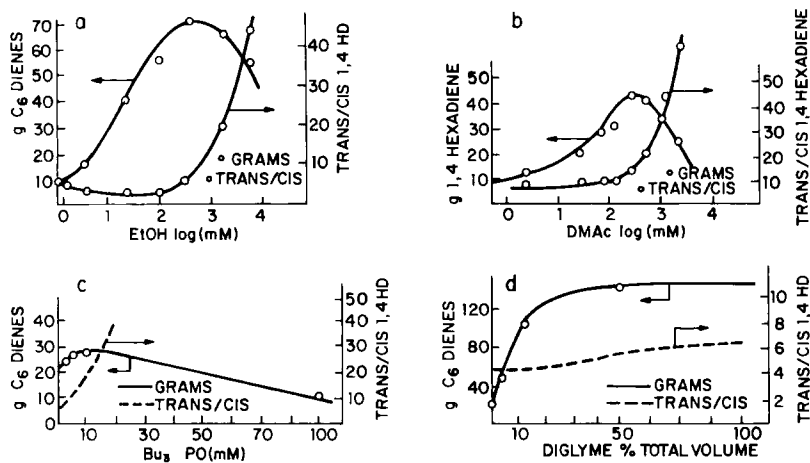


FIG. 5. Effect of donor concentration on rate and trans/cis ratio of 1,4-hexadiene synthesis. Graph a: ethanol; 1 mmole Rh; 2 mmoles HCl; reaction time, 15 minutes. Graph b: $\text{CH}_3\text{C}(\text{O})\text{N}(\text{CH}_3)_2$; 1 mmole Rh; reaction time, 15 minutes. Graph c: $(\text{C}_4\text{H}_9)_3\text{PO}$; 1 mmole Rh; 2 mmoles HCl; reaction time, 60 minutes. Graph d: diglyme; 1 mmole Rh; reaction time, 60 minutes.

0 can increase the catalyst activity when used in suitable quantities. This group can be further divided as follows: Donors with a pK_a value between -5 and -2 enhance the activity regardless of the quantity used; donors with pK_a between -2 and 0 enhance the catalyst activity when present in limited quantity but slow down the reactions when present in larger quantity; and very strong donors, such as pyridine or amines, deactivate the catalyst completely when present in equal molar quantity as the catalyst (25a).

2. Effect of Solvating Ligands on Stereoselectivity

Alderson (1) had observed that the amount of alcohol present strongly influences the ratio of the *trans*- to *cis*-diene formed. With little or no alcohol, the trans/cis ratio is less than 5; in the presence of a large excess of alcohol, the trans/cis ratio rises to 10 or 20.

Su and Collette found that oxygen donors with pK_a values between -2 and 0 are capable of increasing the trans/cis ratio of the 1,4-hexadiene formed. The effect on the trans/cis ratio is again proportional to donor strength and donor concentration.

For example, when a relatively weak donor, such as alcohol, was used,

a donor/catalyst ratio of 1000 was required to bring about an appreciable increase in the trans/cis ratio. When a strong donor such as Bu_3PO was used, a donor/catalyst ratio of only 5 was needed to bring about the same change. Donors with pK_a values of less than -2 , such as ethers or ketones, are too weak to cause any appreciable change in the trans/cis ratio. The extent of change in the trans/cis ratio with changing donor concentration can be seen in Fig. 5 and is summarized in Table VII. Water is a very effective donor for improving the trans/cis ratio, but its effect can be realized only when it is used in a medium in which it is soluble, such as glyme.

No correlation was observed between the dipole moment of the additive and its effect on the stereoselectivity. Thus, CH_3CN , whose dielectric constant, 35, is about the same as that of CH_3OH , has no effect on the trans/cis ratio of the product. On the other hand, octanol, whose dielectric constant is less than 10, is about as effective as CH_3OH in affecting the stereoselectivity.

It becomes quite clear from the above results that there are two types of donors that can affect the catalytic properties of the Rh catalyst. First, there are the weaker donors (pK_a -5 to -2) which are effective in improving the reaction rate but ineffective in increasing the stereoselectivity toward the formation of the trans isomer of 1,4-hexadiene. Second, there are the stronger (pK_a -2 to 0) donors which can enhance both the

TABLE VII
EFFECT OF VARIOUS DONORS ON THE RATIO OF *trans/cis* HEXADIENE

Donors	pK_a	Donor/Rh ^a	Relative effectiveness ^b
None	—	—	0
Acetone	-7.2	—	0
$\text{CH}_3\text{COOC}_2\text{H}_5$	-6.5	—	0
Diglyme (or ethers)	$(-3 \text{ to } -4)$	—	0
CH_3OH	-2	1000	1
H_2O^c	$\sim(-1.9)$	250	4
$\text{CH}_3\text{C}=\text{O}-\text{N}(\text{CH}_3)_2$	-0.5	50	20
Bu_3PO	~ 0	5	200
$[(\text{CH}_3)_2\text{N}]_3\text{PO}$	~ 0	5	200

^a Donor to Rh ratio required to bring about a T/C of 13–15 ($>92\%$ *trans*).

^b Relative effectiveness in forming a T/C ratio of >13 . This equals 1000

[Donor/Rh]

^c Reaction carried out in diglyme.

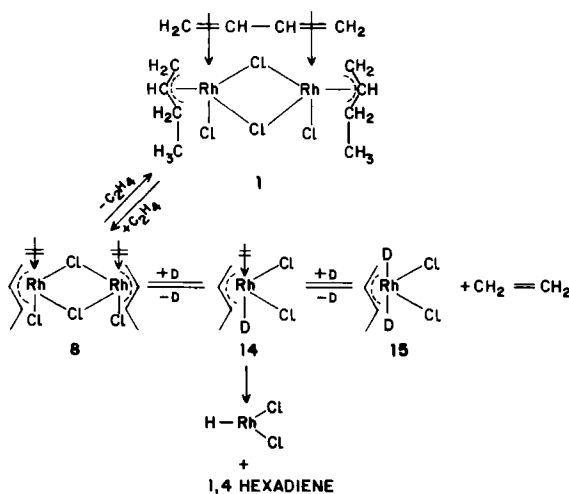
^d Did not give the high T/C ratio regardless of concentration.

rate and the stereoselectivity. It should also be noted that the weaker donors which fail to enhance the stereoselectivity also fail to inhibit the catalytic activity at higher concentrations, while the stronger donors that improve the stereoselectivity also inhibit the catalytic reaction at higher concentrations (compare curves a, b, and c with curve d in Fig. 5).

3. Speculation on the Ligand Effect in the Light of Reaction Mechanism

a. Effect on Catalyst Activity. The interaction of the Rh catalyst with electron donors in nonpolar media is represented in Scheme 5. Before the addition of the donors, the Rh^{III} complex is expected to assume the dimeric structure **8**. Addition of a suitable electron donor, D, converts the dimer first into the monomeric form **14** and then into **15**.

The effect of donors on the catalyst activity can be explained by assuming that the dimeric complex is not an active catalyst (Cramer's kinetics indicate a monomeric Rh species as active catalyst; see Section II,B,2) and that **14** with a free coordination site for ethylene is the active catalyst, while **15** with both coordination sites occupied by donors is catalytically inactive. When D is a weak donor, such as ketone or ether (see Fig. 5d), the reaction rate increases, slowly reaching a maximum and leveling off at the maximum as the concentration of the donor is increased. It can be speculated that these donors interact with the catalyst only to the extent that they break up the dimer **8** to form **14**, but that

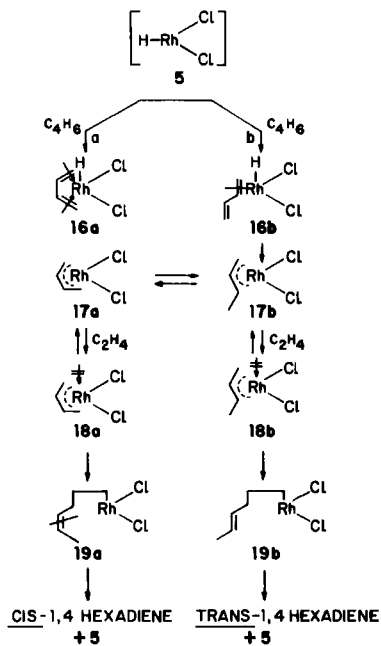


SCHEME 5. Donor effect on rate of reaction.

they do not compete with ethylene for a second coordination site to form complex **15**. On the other hand, with stronger donors, such as alcohol or dimethylacetamide (see Fig. 5a–5c), the reaction rate increases rapidly with increasing donor concentration, reaches a maximum, and then decreases with addition of more donors. This indicates that these donors not only break up the dimer **8** to form **14** but further react with **14** to form **15** at high donor concentration. The point of maximum activity will be a function of the ability of the donors to compete with ethylene for the coordination site on **14**.

b. The trans/cis Ratio of 1,4-Hexadiene. The catalytic cycle in Scheme 2 can be expanded into Scheme 6 to take into consideration the stereoselectivity in the formation of either *trans*- or *cis*-1,4-hexadiene. In this catalytic scheme, the steps in the left-hand column represent the series of reactions leading to the formation of the *cis* isomer; those in the right-hand column lead to the *trans* isomer.

The key intermediates in the formation of both *cis*- and *trans*-1,4-hexadienes are the *anti*- π -crotyl rhodium **17a** and the *syn* isomer, **17b**. The ratio of *trans*/*cis* products is determined by (a) the ratio of **17b** to



SCHEME 6. Donor effect on *trans*/*cis* ratio.

17a initially formed as a result of the reaction of cisoid- or transoid-coordinated butadiene with the rhodium hydride **5**, and (b) the extent of isomerization of **17a** to the more stable **17b** prior to reaction with ethylene to form the C₆ species. It has been speculated that the electron donors increase the trans/cis ratio by creating a situation favoring the formation of **17b** as follows: First, by coordinating with the catalyst center, it forces the butadiene to coordinate as a monodentate or the transoid structure. Second, it can compete with the ethylene coordination step (i.e., the forward reaction **17a** → **18a**), allowing more time for **17a** to isomerize to **17b**. The possibility of this competition reaction, which is also represented by the equilibrium between **14** and **15** in Scheme 5, can be demonstrated readily by carrying out reactions at different ethylene concentrations. At very low ethylene concentration, we expect a slowdown of the forward reaction **17a** → **18a**, allowing more time for the isomerization **17a** → **17b**; thus, a higher trans/cis ratio should result compared to that produced at high ethylene concentration. This is exactly what was found, as shown in Table VIII. This table shows that a trans/cis ratio of 3 can be raised to 22 by reducing the ethylene pressure from 6.8 to 0.68 atm in the reactor. Of course, the rate of reaction was also reduced accordingly. A third possibility of the donor effect is that it might increase the rate of the isomerization **17a** → **17b**.

The data at hand are insufficient to resolve the relative importance of these factors. It is important to note that the only donors that affect the isomer distribution also reduce the reaction rate at higher donor concentrations and that the enhancement in the trans/cis ratio begins not right

TABLE VIII
EFFECT OF CHANGE OF ETHYLENE PRESSURE
ON THE RATIO OF *trans*- TO *cis*-HEXADIENE
AND REACTION RATES^a

Pressure (atm ^b)	trans/cis ratio	Rate (g 1,4- hexadiene/15 min)
0.68	22	2-3
1.36	17	—
2.04	11	8
6.8	3	41

^a The reaction was carried out in the presence of small amount of alcohol, not enough to enhance the trans/cis ratio.

^b Derived from the difference in reactor pressure before and after the introduction of ethylene.

away but near the point where the enhancement of the rate reaches a maximum. This might suggest that the donors merely reduce the rate of the insertion reaction ($17a \rightarrow 19a$). There is, however, no simple correlation between reaction rate and the trans/cis ratio, for we must take into consideration the change in concentration of all the species involved in Scheme 5 as a result of varying the donor concentrations in the reaction mixture.

The complex relationship between rate and trans/cis ratio can be appreciated further by examining the plot in Fig. 6. Curve a represents runs carried out at constant but low ethanol concentration and increasing ethylene pressure; the drop in trans/cis with increasing rate has been discussed above. Curve b in Fig. 6 is from reactions carried out at constant ethylene pressure and increasing donor concentration. The trans/cis ratio is at first unchanged while the reaction rate almost doubles; then the ratio abruptly rises while reaction rate stays constant; finally, it continues to rise as reaction rate falls.

4. Donor Effect on Isomer Distributions

Although the reactions in the above ligand effect studies are designed to minimize the formation of isomers of 1,4-hexadiene, approximately 10% isomers are still formed. These are 3-methyl-1,4-pentadiene and 2,4-hexadiene and a very small amount of higher oligomers. Whatever effect the donor might have on the rate of formation of these isomers (i.e., with respect to the 1,4-hexadiene formation) or on their distributions appeared to be insignificant (24).

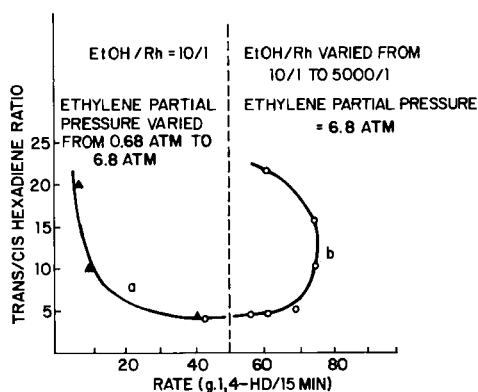


FIG. 6. *trans/cis* Hexadiene ratio vs. initial reaction rate at variable ethylene pressures and ethanol concentrations.

III

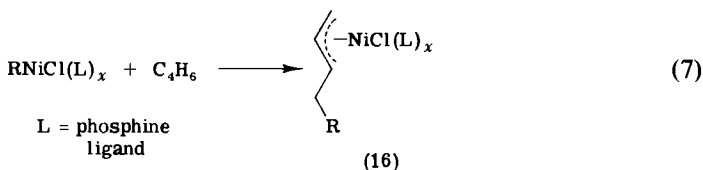
Ni-BASED CATALYST SYSTEM

A. Background

Ni complexes have been used extensively as catalysts for olefin transformations. Some examples are propylene dimerization (26, 27), butadiene oligomerization and cyclooligomerization (28, 29), butadiene ethylene cooligomerization (27), and butadiene polymerization (30, 31). When conjugated dienes are involved, π -allylic Ni-type complexes become the predominant intermediate, and the structure and geometry of this intermediate become the factors that determine the structure or stereoorientation of the final product formed. The work of Wilke and co-workers (27–29, 32–34) is especially noteworthy. They were the first to coreact ethylene and butadiene to form 1:2 adducts (27, 28), i.e., 1,4,9-decatriene and 1,5-cyclooctadiene, using zero-valent Ni complexes as catalyst. Such a catalyst can be generated *in situ* if desired by interaction of organometallic compounds, such as R_3Al , with a nickel salt in the presence of weak olefinic ligands such as cyclooctadiene or cyclodecatriene. Kealy, Miller, and Barney (35, 36) found that an *in situ*-generated catalyst derived from R_2AlCl and $(R_3P)_2NiCl_2$, under about the same conditions (mild) as the 1,2-cooligomerization, will instead produce predominantly a 1:1 codimer, i.e., 1,4-hexadiene. It is interesting to note that, although this nickel-based catalyst system is very different from the Rh system described in Section II, the major product and by-products formed are in general the same; and this suggests that they might have functionally very similar catalyst intermediates.

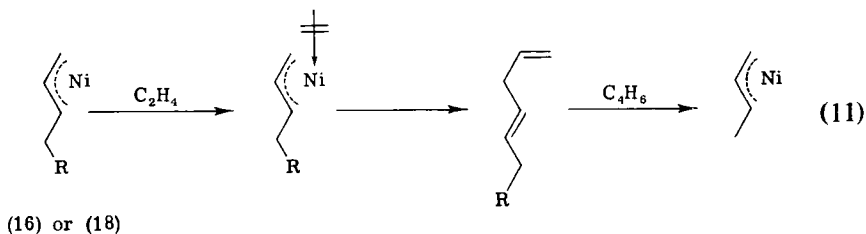
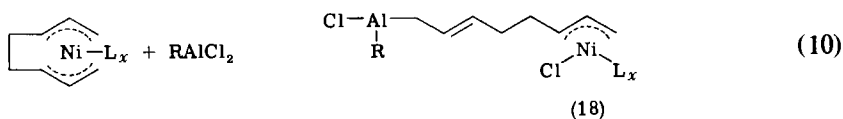
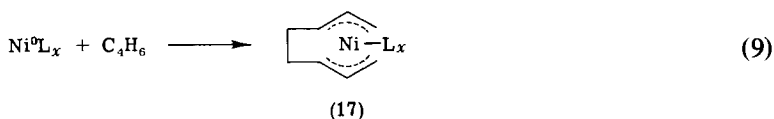
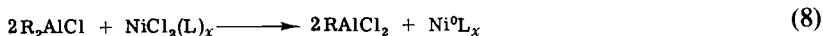
B. Catalyst Formation and Reaction Mechanism

The catalytic system described by Kealy is expected to undergo a series of interactions among its various components before generating



the active catalyst. The observed induction period in the beginning of the reaction is consistent with this expectation. The chemistry of the initial reactants in the catalyst system suggests two possible paths to the formation of the active species. The first path is represented by Eqs. (6) and (7), in which the nickel chloride is first alkylated and then reacted with butadiene to form a π -allylic species (16).

The second pathway is represented by Eqs. (8)–(11). These reactions involve reduction of the Ni^{II} halide to a Ni^0 complex in a manner similar to the generation of Wilke's "bare" nickel (37, 38) which can form a C_8 bis- π -alkyl nickel (17) in the presence of butadiene [Eq. (9)]. It is reasonable to assume that in the presence of excess alkylaluminum chloride, an exchange reaction [Eq. (10)] can take place between the Cl^- on the aluminum and one of the chelating π -allyls to form a mono- π -allylic species 18. Complex 18 is functionally the same as 16 under the catalytic reaction condition and should be able to undergo additional reaction with a coordinated ethylene to begin a catalytic cycle similar to Scheme 4 of the Rh system. The result is the formation of a 1,4-diene derivative similar to 13 and the generation of a nickel hydride which then interacts with a butadiene to form the ever-important π -crotyl complex [Eq. (11)].



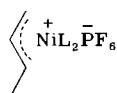
If the second pathway is possible, then one should be able to use a Ni^0

complex instead of a Ni^{II} complex in the catalyst system. This is indeed true, as shown by Su and Collette (39), and shall be discussed in more detail in Section III,C.

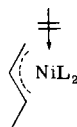
The essential steps in the nickel-catalyzed 1:1 codimerization reaction, which involve hydride addition to butadiene and ethylene coordination to the metal atom, were first proposed by Kealy, Miller, and Barney (35) and were later demonstrated by Tolman (40) using a model complex. Tolman prepared the complex $\text{H}-\text{Ni}^+\text{L}_4\text{PF}_6^-$ [$\text{L} = (\text{EtO})_3\text{P}$] and showed that, after prior dissociation to form $\text{H}-\text{NiL}_3$, it can react with butadiene to form a π -crotyl complex **19**.



(19)



(20)

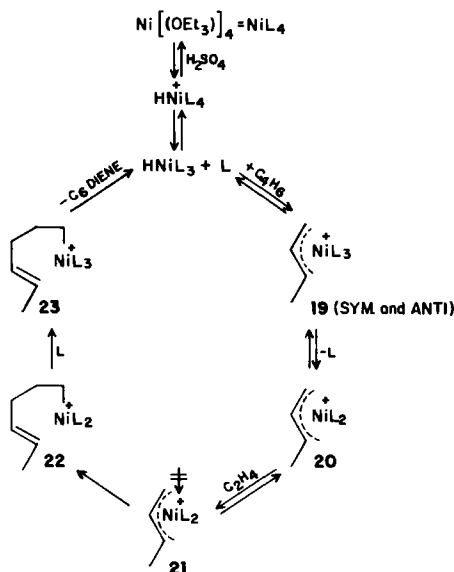


(21)

A tetracoordinated complex (**20**)⁴ was actually isolated. Complex **20** in the presence of ethylene forms the coordinated complex **21**, as can be seen from ^1H NMR. Complex **21** is a model of the intermediate for the additional reaction to form C_6 dienes. The model catalyst had been shown to be a codimerization catalyst under more severe conditions (high temperature), although the rate of reaction was very slow compared to the practical systems. These studies are extremely useful in demonstrating the basic steps of the codimerization reactions taking place on the Ni atom. The catalytic cycle based on these model complexes as visualized by Tolman is summarized in Scheme 7. A more complete scheme taking into consideration by-product formation can be found in Tolman (40).

The sequence of reactions in Scheme 7 is generally similar to that depicted in Scheme 2, except that the ligand seems to play an important

⁴ Assume the π -crotyl group occupies two coordination sites.



SCHEME 7. Nickel-catalyzed codimerization—model system. Data from Tolman (40).

role here in promoting the release of the C_6 diene and regenerating the metal hydride, i.e. $22 \rightarrow 23 \rightarrow \text{HNiL}_3$. It is interesting to note that an analogous role was played by butadiene in the Rh catalyst system (see Scheme 3). The slow rate of reaction for these complexes can be attributed to the larger equilibrium constant between 20 and 19.

It should be noted here again that the catalytic reaction does not involve a change of valence of the metal. In general, catalytic olefin addition reactions that involve a hydride transfer do not require change of valence in the metal catalyst. On the other hand, carbon-carbon bond formation by coupling reactions which involve electron shifts, such as in Wilke's Ni^0 -catalyzed butadiene oligomerization reaction [Eq. (1)], requires a valence change on the metal.

C. Factors Affecting Catalyst Activity and Selectivity

Though the models discussed above have great mechanistic value, the catalytic properties are complicated by the presence of cofactors, such as the structure of cocatalyst and the nature of the phosphine ligands. The effect of these cofactors on the catalytic properties can be used to optimize the catalyst activity or to direct the course of the reactions. To

determine these factors, Su and Collette (39) have reinvestigated the catalytic reaction by using a three-component catalyst system represented in general by $\text{Ni}^0(\text{COD})_2 + \text{R}_3\text{P} + \text{R}_x\text{AlCl}_{3-x}$, where COD is cyclooctadiene and $\text{Al/Ni} \approx 5$. The possibility of generating an active catalyst from a Ni^0 complex is described in Eqs. (8)–(10). The reactions were carried out under mild conditions in the presence of excess butadiene under pressure. The $\text{Ni}^0(\text{COD})_2$ is soluble in toluene, and the effect of the aluminum cocatalyst and the phosphine ligands can be observed by product analysis.

The above catalyst system is long-lived; and like the Miller catalyst, it formed primarily 1,4-hexadiene, 3-methyl-1,4-pentadiene, and 2,4-hexadiene from ethylene and butadiene. A typical distribution of products formed by this catalyst and by the $(\text{Bu}_3\text{P})_2\text{NiCl}_2/\text{i-Bu}_2\text{AlCl}$ catalyst is shown in Table IX. The improved conversion and yield can be attributed to a better cocatalyst system, as shall be discussed later. Su and Collette's studies are summarized in the following discussions.

1. Catalyst Activity

a. The Phosphine Ligand Effect. For the catalyst system described above, it was found that only one phosphine per nickel atom is required for maximum activity. In the presence of more than one phosphine per nickel, the catalyst will remain active only if the molar quantity of the aluminum cocatalyst exceeds that of the phosphine. Bidentate phosphines such as $\text{Ph}_2\text{PCH}_2\text{—CH}_2\text{—Ph}_2$ inhibit the catalyst activity (as much as several hundredfold reduction in rate) even in the presence of excess aluminum cocatalyst. This chelating ligand inhibition effect has also been observed by Hata (26) and Wilke (27) in the Ni-catalyzed dimerization of

TABLE IX
CATALYTIC SYNTHESIS OF 1,4-HEXADIENE BY Ni CATALYST^{a,b}

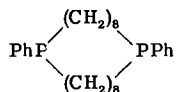
Catalyst	BD ^b conv.	1,4-HD ^b (%)	T/C ^b	3-MeP ^b	2,4-HD ^{b,c} (%)	Higher-boiling olefins (%)
i-BuAlCl ₂ + Ni ⁰ COD ₂ + Bu ₃ P	77	69	~	8.1	8.2	~15
i-Bu ₂ AlCl + (Bu ₃ P) ₂ NiCl ₂	33	65	~2.5	8	3–4	~22

^a Catalyst ratio Ni/Al/P = 1/5/1; reaction time, 60 minutes.

^b BD = butadiene; 1,4-HD = 1,4-hexadiene; T/C = ratio of *trans*-1,4- to *cis*-1,4-hexadiene; 3-MeP = 3-methyl-1,4-pentadiene; 2,4-HD = 2,4-hexadiene.

^c The yield of 2,4-hexadiene increases with increasing conversion.

propylene. However, a bisphosphine with long methylene chain in between,



behaves as a monophosphine because it has lost the strong chelating property. The above result indicates that the active species prefer only one phosphine on the Ni atom. The electronic properties of the phosphines themselves also affect the rate of reaction. In general, the rate increases with more electropositive phosphines (see Table X, column 5).

b. Cocatalyst Structure and Catalyst Activity. The aluminum cocatalysts contribute very significantly to the reaction property of the catalyst system.

During the catalyst activation reactions in Kealy's catalyst system discussed above [Eqs. (6)–(7) and (8)–(10)], a monoalkylaluminum chloride is formed. Because the initial dialkylaluminum chloride R_2AlCl is present in excess, the effective cocatalyst could be the original R_2AlCl or the RAlCl_2 formed during the reaction. To clarify the role of the aluminum component in the actual codimerization reaction the following catalyst combinations have been tested:

- (a) $\text{Ni}[\text{COD}]_2 + \text{Ph}_3\text{P} + i\text{-Bu}_3\text{Al}$
- (b) $\text{Ni}[\text{COD}]_2 + \text{Ph}_3\text{P} + i\text{-Bu}_2\text{AlCl}$
- (c) $\text{Ni}[\text{COD}]_2 + \text{Ph}_3\text{P} + i\text{-BuAlCl}_2$
- (d) $\text{Ni}[\text{COD}]_2 + \text{Ph}_3\text{P} + i\text{-Bu}_2\text{AlCl} + \text{BuAlCl}_2$

Catalyst (a) was inactive; catalyst (b) had low activity; catalyst (c) is very active. The much greater activity of $i\text{-BuAlCl}_2$ as a cocatalyst over $i\text{-Bu}_2\text{AlCl}$ is shown in Fig. 7. Figure 7 also shows that the activity of catalyst system (b) can be increased to nearly that observed with catalyst system (c) by addition of some $i\text{-BuAlCl}_2$, i.e., formation of catalyst system (d).

The above results indicate that the monoalkylaluminum chloride rather than the dialkylaluminum chloride is the more effective cocatalyst. The relatively high activity of Kealy's catalyst can be attributed to the *in situ* formation of RAlCl_2 as a result of reduction of Ni^{II} by the dialkylaluminum chloride. However, such reduction is not possible in the $\text{R}_2\text{AlCl}/\text{Ni}^0$ catalyst system. Thus, the differences between RAlCl_2 and R_2AlCl can be readily compared with the Ni^0 catalyst systems.

Monoalkyl- and dialkylaluminum chloride differ not only in their Lewis acidity but in their alkylation ability. However, in the above experiment,

TABLE X
THE INFLUENCE OF PHOSPHINE LIGANDS ON THE CODIMERIZATION REACTION WITH
 $\text{Ni}[\text{COD}]_2$ AND $i\text{-BuAlCl}_2$

R_3P	$\nu(\text{CO})^c$ (A_1)	T/C ^a	3-MeP ^a (%)	Rel. react. rate ^b	1,4-HD ^b (%)
$(\text{C}_6\text{H}_{11})_3\text{P}$	2056.4	1.5	17.0	2.0	83
Bu_3P	2060.3	2.0	14.0	1.25	82
Allyl_2PhP	2065.3	2.9	8.0		
Ph_3P	2068.9	4.0	8.0	1.0	80
$(m\text{-CF}_3\text{C}_6\text{H}_4)_3\text{P}$	2074.1	5.0	7.5		
$(\text{C}_6\text{F}_5)_2\text{Ph}_2\text{P}$	2074.8	6.0	6.0	0.7	60

^a The isomer distributions were measured at <25% butadiene conversion. T/C = trans/cis ratio of 1,4-hexadiene; 3-MeP=3-methyl-1,4-pentadiene.

^b Relative rates were measured by the time required to achieve 43% conversion of butadiene under the same reaction conditions. Yield of 1,4-hexadiene at 43% conversion of butadiene.

^c Tolman (44).

because alkylation on $\text{Ni}^0(\text{COD})_2$ is unlikely, the difference in activity between RAlCl_2 and R_2AlCl can only be attributed to the difference in their Lewis acidity. The importance of Lewis acidity is further confirmed by testing AlBr_3 as cocatalysts. The composition $\text{Ni}[\text{COD}]_2/\text{Ph}_3\text{P}/\text{AlBr}_3$ did indeed prove to be a very active codimerization catalyst, but the reaction was complicated by considerable polymerization of butadiene and by a much more extensive isomerization of 1,4- to 2,4-hexadiene:

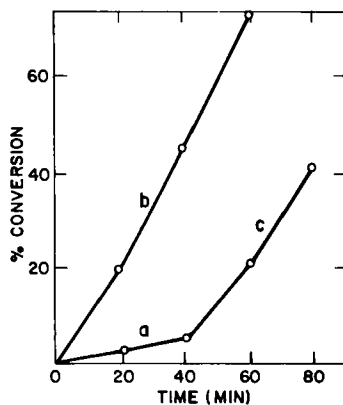


FIG. 7. Cocatalyst effect on nickel catalyst systems. Curve a, $\text{Ni}^0\text{COD}_2 + \text{Ph}_3\text{P} + \text{Si-Bu}_2\text{AlCl}$; curve b, $\text{Ni}^0\text{COD}_2 + \text{Ph}_3\text{P} + \text{Si-BuAlCl}_2$; curve c, addition of 2i-BuAlCl_2 to (a) after 40 minutes of reaction.

Both of these may be caused by excess free AlBr_3 . By using a Ni^{II} complex with a more basic phosphine, $(\text{Bu}_3\text{P})_2\text{NiCl}_2$, and by limiting the level of AlBr_3 to 2–3 equivalents per nickel, it was possible to prepare 1,4-hexadiene with reasonable yield at low conversions. The activity of this system in forming C_6 dienes exceeded the corresponding $i\text{-BuAlCl}_2$ catalyst system, but the selectivity in forming 1,4-hexadiene was considerably lower. On the other hand, the ineffectiveness of a trialkylaluminum R_3Al as cocatalyst could be attributed to the low Lewis acidity of the cocatalyst. However, other factors cannot be dismissed; e.g., chloride may be lacking in the catalyst system to form a bridge complex, or the cocatalyst may be too strong a reducing agent, which prevents the Ni from attaining the active Ni^{II} valence.

The Lewis acidity of the aluminum cocatalyst can also be reduced by forming a complex with electron donors, such as ethers. It was found that in the presence of a slight excess of diethyl ether the activity of the catalyst $\text{AlCl}_3 + \text{Ni}^0\text{COD}_2 + \text{R}_3\text{P}$ was greatly reduced, while no significant change in activity occurred in the presence of a corresponding amount of the more weakly basic diphenyl ether. Table XI lists the relative catalyst activity of various types of Al cocatalysts.

c. Model of an Active Catalyst. The above results related to the influence of phosphine ligands and the Al cocatalyst on the catalytic properties indicate that a desirable catalyst system consists of a 1:1 Ni phosphine

TABLE XI
RELATIVE RATE OF HEXADIENE SYNTHESIS USING VARIOUS
ALUMINUM COCATALYSTS WITH $\text{Ni}[\text{COD}]_2 + \text{Ph}_3\text{P}$

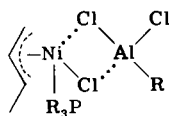
Aluminum cocatalyst ^a	Relative rate ^b
$i\text{-Bu}_3\text{Al}$	0, inactive
R_2AlOR	0, inactive
$i\text{-Bu}_2\text{AlCl}$	<1
$i\text{-BuAlCl}_2$	10
AlBr_3^c	Fast but complicated
$i\text{-BuAlCl}_2(\text{PhOPh})$	7–9
$i\text{-BuAlCl}_2[\text{Et}_2\text{O}]$	<1
EtAlCl_2	<10
$\text{EtAlCl}_2 + \text{Et}_2\text{AlB}(\text{B}=\text{OR}, \text{NR}_2)$	1–5

^a No change in trans/cis ratio can be observed when the same R_3P was used except in the case of Et_2AlB .

^b Rate measured at butadiene conversion less than 25%.

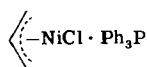
^c Produce both C_6 dienes and polymeric butadiene even at low conversion of butadiene.

complex coupled with a monoalkylaluminum dichloride. Thus, a catalyst complex that imparts the best activity can be conceived to resemble structure **24** with a phosphine tightly bonded to the Ni atom, which is linked to the cocatalyst through the chloride bridges.



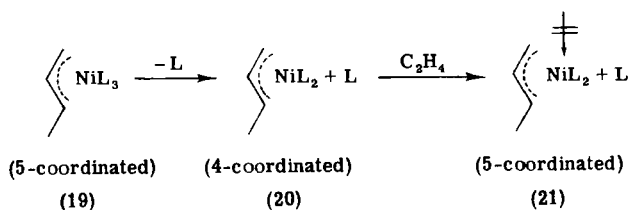
(24)

The bimetallic structure is essential, for the complex

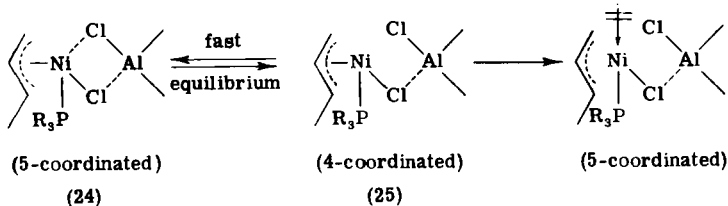


which seems to contain all the requirements as catalyst for the dimerization reaction, is almost inactive by itself under the codimerization conditions. Upon addition of RAlCl_2 , it instantly becomes the most active catalyst.

Catalytic cycles resembling that of Tolman can be applied using **24** as reaction center. Tolman's model shows that the coordination number on the Ni atom changes between 4 and 5 (see Scheme 7) during the following catalytic reaction:



It is conceivable that analogous changes also take place here but probably more efficiently, because the ligand dissociation step involved only weakly bonded bridging Cl^- rather than a relatively strongly coordinated phosphite ligand:



In Tolman's model ethylene must compete with the strong phosphite ligand for a coordination site, while in the case of the bimetallic complex it only has to compete with a weak chloride ligand. The very high activity of the bimetallic complex (24) as compared to the model complex (21) might be explained in part by this difference.

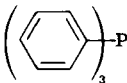
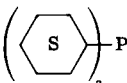
2. Effect on Stereoselectivity of 1,4-Hexadiene Synthesis

In Section II, we discussed the influence of solvating ligands on the selectivity or trans/cis ratio in the Rh-catalyzed 1,4-hexadiene synthesis. In the case of nickel catalyst, the trans/cis ratio is also subject to change; however, the types of solvating ligands that influence the Rh system are generally not applicable to the Ni system, because any ligand that might be strong enough to influence the stereoselectivity by solvation tends to destroy the bimetallic complex. The major influences on the stereoselectivity of the nickel catalyst arise instead from the structural effect of the phosphine ligand and the Al cocatalyst.

a. The Phosphine Ligands. Types of phosphines used in the catalyst system have a definite effect on the trans/cis ratio of the 1,4-hexadiene formed; for example, when Bu_3P is used, trans/cis is about 2, but when Ph_3P is used, trans/cis increases to 4. Because Ph_3P differs from Bu_3P both electronically and sterically from the ligand point of view, the change of the trans/cis ratio could be due to an electronic as well as a steric effect. This existence of a steric effect can be determined by comparing phosphine ligands of increasing size.

In Table XII three phosphines of very different sizes are compared for

TABLE XII
STERIC EFFECT ON STEREOSELECTIVITY

	Ligand cone angle ^a	trans/cis ratio
$(\text{C}_4\text{H}_9)_3\text{P}$	$130^\circ \pm 4^\circ$	2.0
	$145^\circ + 2^\circ$	4.0
	$179^\circ \pm 10^\circ$	1.5

^a Tolman (41).

their effect on the trans/cis ratio of the hexadiene produced. The relative size of the phosphine is based on the measurement of the ligand cone angle. This method was designed by Tolman (41) for a semiquantitative measure of steric dimension of the phosphines.⁵ The ligand cone angle can be measured directly from atomic models. As can be seen in Table XII, no correlation or trend can be observed to indicate that the steric size is a significant factor in determining the stereo preference. This suggests that the electronic effect of the phosphine is the factor to consider.

It is well understood that phosphines can donate electrons to the metal to form σ bonds and can expand their 3d orbitals to accept electrons from the metal in the form of π bonding. The electronic effect is thus related to the donor-acceptor properties of the phosphine ligands. The acceptor property can be elucidated by comparing the C=O stretching frequency of Ni phosphine carbonyl complexes (43, 44); i.e., acceptor properties are proportional to $\lambda_{\text{CO}}(A_1)$ of $\text{R}_3\text{P}-\text{Ni}(\text{CO})_3$. The higher the frequency, the stronger the acceptor properties. This electronic effect is demonstrated in Table X, in which the phosphines are arranged vertically in order of increasing acceptor properties. This increase in acceptor properties is reflected in the C=O stretching frequency of the corresponding phosphine-substituted nickel carbonyl complex. As one can see, there is a steady increase in the trans/cis ratio from 1.5 to 6 as we go from the weakest acceptor, $(\text{C}_6\text{H}_{11})_3\text{P}$, to the strongest acceptor, $\text{Ph}_2(\text{C}_6\text{F}_5)\text{P}$.

With even stronger acceptor ligands, e.g., $\text{Ph}(\text{C}_6\text{F}_5)_2\text{P}$ or $(\text{C}_6\text{F}_5)_3\text{P}$, the catalyst lost its property as a hexadiene catalyst and became instead primarily a catalyst for oligomerization of butadiene. This might be due to the fact that the basicity or donor property of these strong acceptors becomes too weak to effectively bond to the Ni atom, making it behave as if no phosphine is present.

Figure 8 shows a plot of the CO stretching frequency vs. the trans/cis ratio. A good linear plot is obtained. As one can see, the electronic effect exerted by the phosphine ligands on trans/cis is real. Unfortunately, there is a limit as to how far one can take advantage of this effect to further increase the stereoselectivity.

It is interesting to note that the increase in the ratio as a result of increasing the electron-acceptor property of the phosphines also resulted in a decrease in the production of the 1,2-addition product, 3-methyl-1,4-pentadiene (see Table X). No attempt has been undertaken to explain this observation.

⁵ An excellent review of steric effect of phosphorus ligands on catalytic reaction has been written by Tolman (42).

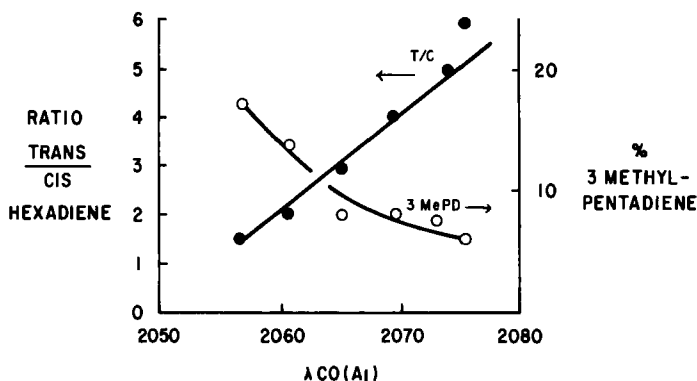


FIG. 8. Effect of phosphine on isomer distribution.

b. Effect of the Aluminum Cocatalyst. As mentioned earlier, the Lewis acidity of the Al cocatalyst greatly affects the rate of the reaction (see also Table XI). However, in general, the change in Lewis acidity or even the change in the alkyl or halide groups on the cocatalyst has no effect on the trans/cis ratio of the hexadiene formed. It was therefore rather surprising to find that the ratio increased (regardless of the types of R_3P use) when the cocatalysts were derived from a suitable combination of alkylaluminum halides and an alkylaluminum alkoxide or amide,

TABLE XIII
EFFECT OF THE RATIO OF $R_nAlCl_{3-n}/R_mAlB_{3-m}$ ON THE
trans/cis RATIO OF 1,4-HEXADIENE^a

Phosphine	Aluminum cocatalyst	trans/cis Ratio
Ph_3P	$EtAlCl_2$	4–4.5
Ph_3P	$EtAlCl_2 + Et_2AlOEt$	4–4.5
Ph_3P	$EtAlCl_2 + 2Et_2AlOEt$	6–7
Ph_3P	$EtAlCl_2 + 3Et_2AlOEt$	6–7
Ph_3P	$EtAlCl_2 + 2i-Bu_2AlNEt_2$	6
$C_6F_5PPh_2$	$EtAlCl_2$	6
$C_5F_5PPh_2$	$EtAlCl_2 + Et_2AlOEt$	6
$C_6F_5PPh_2$	$EtAlCl_2 + 1.5Et_2AlOEt$	15–19
$C_6F_5PPh_2$	$EtAlCl_2 + 2Et_2AlOEt$	10–12
$C_6F_5PPh_2$	$2i-Bu_2AlCl + EtAl(O-Pr)_2$	10
$C_6F_5PPh_2$	$EtAlCl_2 + 2i-Bu_2AlNEt_2$	10

^a Catalyst $Ni(COD)_2$.

R_nAlB_{3-n} ($B = OR$ or NR_2). As can be seen from Table XI, the above combination also caused a substantial drop in the catalyst activity, which is expected with a lower overall Lewis acidity of the mixed cocatalyst. The effect of these cocatalysts on the *trans/cis* ratio of the product is very dependent on the ratios of the two aluminum components. The combination which enables the catalyst system to produce the highest proportion of *trans*-hexadiene had $R_2AlB/RAICl_2 = 1.5-2$ (Table XIII).

This narrow range for the effective ratio led to a more detailed examination of the above cocatalyst mixture. Alkylaluminums are known to exist in varying types as well as degrees of association (45). It seemed reasonable that of all the complexes possible from R_xAlCl_{3-x} and R_nAlB_{3-n} , only one type is effective for increasing the *trans/cis* ratio. Evidence for the formation of such a complex was obtained from an analysis of the 1H NMR spectra of mixtures of $EtAlCl_2$ and Et_2AlOEt shown in Fig. 9. Et_2AlOEt is known to exist exclusively in the dimeric form (46), its 1H NMR spectrum showing four peaks corresponding to the absorption of protons on $Al-CH_2CH_3$ and $Al-OCH_2CH_3$ (Fig. 9B). The NMR spectrum of $EtAlCl_2$, which also exists primarily in the dimeric form through chloride bridges (45, 47), is shown in Fig. 9A.

In Fig. 9C, there is no discernible shift in the 1H resonance, indicating

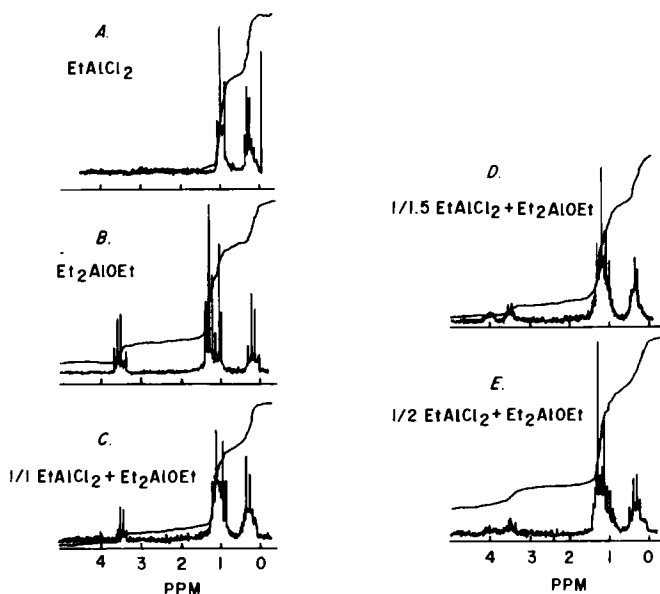
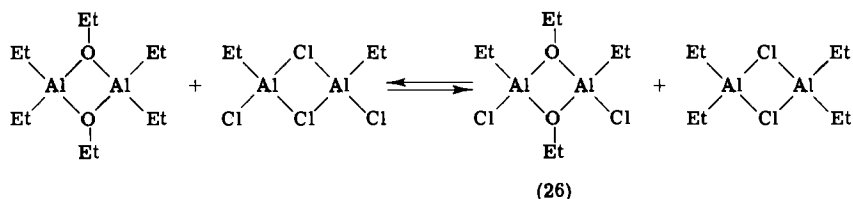


FIG. 9. 1H NMR spectra of $EtAlCl_2$ - Et_2AlOEt catalyst.

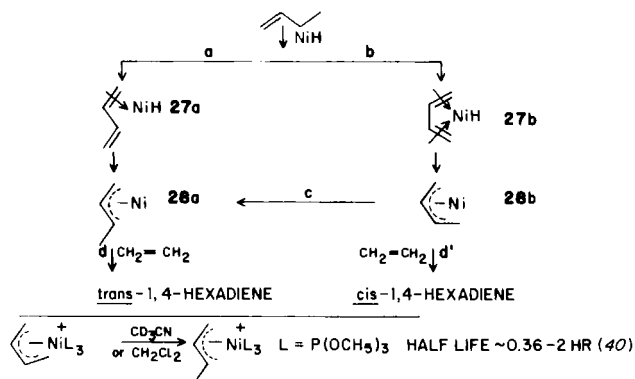
no significant breakup of the original associated structures. At the ratio of 1.5:1 a distinct new peak can be seen at 4 ppm. This new peak grew somewhat when the ratio was increased to 2:1 (Fig. 9D). The 4 ppm peak can be attributed to a new methylene proton absorption as a result of changes imposed on some of the —OEt groups. This downfield shift indicates that the oxygen atom in —OEt has become more electron-deficient (48) than in the original dimeric complex of Et_2AlOEt , and suggests ligand exchange to form a new species with both the Cl and OEt groups bonded to the same Al atom. A very probable reaction might involve a Cl^- and Et^- exchange to form complex **26** and Et_2AlCl :



A small shift in the methyl and methylene absorptions of the $\text{CH}_3\text{CH}_2\text{Al}<$ group on EtAlCl_2 from 1.0 and 0.25 ppm toward the 1.33 and 0.45 ppm region, which is characteristic for the corresponding groups on Et_2AlCl (49), is consistent with formation of some Et_2AlCl in the reaction mixture. A complex such as **26** might be responsible for increasing the trans/cis ratio.

c. Mechanistic Implications. Based on the essential steps discussed earlier, the reaction paths leading to the formation of *trans*- or *cis*-1,4-hexadiene can be represented in Scheme 8, which is more or less analogous to Scheme 6 in Section II for the Rh system.

Reactions **a** and **b** in Scheme 8 represent different ways of coordination of butadiene on the nickel atom to form the transoid complex **27a** or the cisoid complex **27b**. The hydride addition reaction resulted in the formation of either the *syn*- π -crotyl intermediate (**28a**), which eventually forms the trans isomer, or the *anti*- π -crotyl intermediate (**28b**), which will lead to the formation of the cis isomer. Because **28a** is thermodynamically more favorable than **28b** according to Tolman (40) (equilibrium anti/syn ratio = 1:19), isomerization of the latter to the former can take place (reaction **c**). Thus, the trans/cis ratio of 1,4-hexadiene formed is determined by (i) the ratio of **28a** to **28b** and (ii) the extent of isomerization **c** before addition of ethylene to **28b**, i.e., reaction **d'**. The isomerization reaction can affect the trans/cis ratio only when the insertion reaction **d'** is slower than the isomerization reaction **c**.



SCHEME 8. Key reactions controlling stereoselectivity.

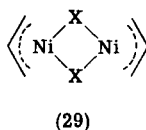
In the model study by Tolman discussed earlier, the half-life of syn-to-anti isomerization measured by ^1H NMR was found to be 0.36 hours at 30°C . This rate of isomerization is far too slow to affect the stereoselectivity of the hexadiene formed with the catalyst considered here. With the bimetallic catalyst, reaction rates frequently approach 4000 molecules of hexadiene/Ni atom/hour at 25°C (or ca. 1 hexadiene/Ni/second). The rate of insertion reaction d' must be at least as fast as this, and the isomerization reaction would have to be even faster to affect the trans/cis ratio of the product.

It is entirely possible that isomerization may proceed much faster with this catalyst than with the model system considered by Tolman. To test this possibility, reactions were run at reduced ethylene concentrations. This should slow down the insertion reaction (d') relative to the isomerization reaction (c). No effect on the trans/cis ratio of the product was observed, while the rate of hexadiene formation was reduced over 200-fold (39). So, unlike the Rh systems, the syn-to-anti isomerization appeared too slow to be a controlling factor for the stereoselectivity.

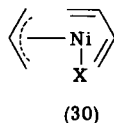
The trans/cis ratio of the product must, therefore, be determined at an earlier reaction stage and most probably by the ratio of species **27a** and **27b**. Steric or electronic factors affecting this ratio will influence the trans/cis ratio of the resulting 1,4-hexadiene. The phosphine and the cocatalyst effect on the stereoselectivity can thus be interpreted in terms of their influence on the mode of butadiene coordination. Some earlier work on the stereospecific synthesis of polybutadiene by Ni catalyst can be adopted to explain the effect observed here, because the intermediates that control the stereospecificity of the polymerization should be essen-

tially the same for the polymerization and the dimerization catalyst, i.e., the π -crotyl type complex.

It has been known that π -allylnickel halides are catalysts for polymerization of butadiene (50, 51). When the halide is chloride, the polymer formed is *cis*-polybutadiene; when the halide is iodide, the polymer is *trans*-polybutadiene. Porri and co-workers (50) interpret this effect in terms of the ease of dissociation of the dimeric complex 29 by butadiene. The chloride complex



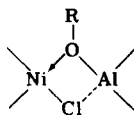
can be split easily by butadiene to form the monomeric complex 30



which has more coordination sites, thus favoring the *cisoid*-coordinated structure and hence the formation of *cis*-polybutadiene.

On the other hand, the iodide complex remains in the dimeric form (29) and has less coordination sites available at the nickel atom. The butadiene is forced into a *transoid*-coordinated structure and thus favors the formation of *trans*-polybutadiene. Another interpretation has been set forth by Dolgoplosk (51) invoking the presence of electronic factor. He argued that iodide has a stronger tendency (as compared to Cl^-) to form multiple bonds with the Ni by accepting electron density from the metal and thus reducing the number of effective bonds which can be formed between the metal and butadiene. Under this situation, the *transoid* coordination becomes favored compared to the *cisoid* coordination. The phosphine effect discussed above appears to be in agreement with the latter interpretation, for a stronger π -acceptor phosphine, which is the counterpart of the iodide, favored the formation of *trans*-1,4-hexadiene. On the other hand, a stronger σ -donor phosphine, which is more like the chloride, produces more *cis* isomer.

The *trans/cis* ratio of hexadiene is also increased by addition of aluminum cocatalysts containing —OR or —NR₂ groups. It is proposed that this is due to selective blocking of a coordination site on the nickel by the formation of an intermediate such as 31, and this too would favor the formation of the *transoid* structure.



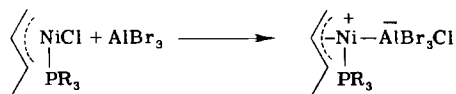
(31)

In the polymerization of butadiene, Teyssie (52–54) has shown that certain electron donors, such as alcohols or phosphines, can convert π -allylnickel chloride from a catalyst which forms *cis*-polybutadiene to one which produces *trans*-polybutadiene. These ligands presumably block a site on the nickel atom, forcing the butadiene to coordinate by only one double bond. While alcohols cannot be added directly to the hexadiene catalyst (as they deactivate the alkylaluminum cocatalysts), incorporation of the oxygen atom on the cocatalyst places it in an ideal position to coordinate with the nickel. The observed rate reduction (52) when the *cis*-polybutadiene catalyst is converted into a *trans*-polybutadiene catalyst is also consistent with the observed results in the 1,4-hexadiene synthesis.

D. Catalyst Structure and Selectivity toward 1:1 Codimerization

The selectivity to form 1:1 codimer with the nickel catalyst discussed here can best be rationalized in terms of the limitations of coordination sites on the nickel atom. Consider the active catalyst structure represented by **24–25** or by **20** (Scheme 7). There are three sites available for coordination, which are just enough to accommodate one π -crotyl group and one ethylene or one hydride and one butadiene. Because of the fact that the maximum coordination number is 5 in the nickel atom (see Scheme 7), two of the coordination sites must be tightly blocked by ligands. In the 1:1 codimerization catalyst this is achieved by the phosphine and the chloride ligand **24**. Any change resulting in the removal of these ligands is expected to transform the catalyst into a butadiene polymerization or oligomerization catalyst. Thus, removal of the phosphine from **24** converts it into a structure which is known (50–56) to be an effective polybutadiene catalyst. This also explains why a catalyst containing weak σ -donor phosphines, e.g., $(\text{C}_6\text{F}_5)_3\text{P}$, is not a good 1:1 codimerization catalyst but rather an oligomerization and polymerization catalyst. As discussed earlier, when a very strong Lewis acid (AlBr_3) is used as a cocatalyst, the catalyst system favors polymerization. This might be caused by the removal of the Cl^- ligand from **24** as a result of

the ionization reaction:



The ionization of π -allylnickel chloride by AlBr_3 during the polymerization of butadiene has also been suggested (50, 56) as the reason for increasing the reaction rate.

The nickel catalyst under the condition for the 1:1 codimerization is not known to dimerize or polymerize ethylene, although a similar catalyst system has been known to dimerize propylene (26, 27) via a π -allyl intermediate.

E. Isomer Distributions

The isomer distribution of the nickel catalyst system in general is similar qualitatively to that of the Rh catalyst system described earlier. However, quantitatively it is quite different. In the Rh system the 1,2-adduct, i.e., 3-methyl-1,4-hexadiene is about 1–3% of the total C_8 products formed, while in the Ni system it varies from 6 to 17% depending on the phosphine used. There is a distinct trend that the amount of this isomer increases with increasing donor property of the phosphine ligands (see Table X). The quantity of 3-methyl-1,4-pentadiene produced is not affected by butadiene conversion. On the other hand the formation of 2,4-hexadienes which consists of three geometric isomers—trans-trans, trans-cis, and cis-cis—is controlled by butadiene conversion. However, the double-bond isomerization reaction of 1,4-hexadiene to 2,4-hexadiene by the nickel catalyst is significantly slower than that by the Rh catalyst. Thus at the same level of butadiene conversion, the nickel catalyst produces significantly less 2,4-hexadiene (see Fig. 2).

The Ni catalyst system derived from $\text{R}_2\text{AlCl} + \text{NiCl}_2(\text{R}_3\text{P})_2$ was found by Miller (57, 58) to be capable of catalyzing the skeletal arrangement of 3-methyl-1,4-hexadiene to form other dienes including the reversal product, *cis*-1,4-hexadiene. *cis*-1,4-Hexadiene was also found to undergo rearrangement to form *trans*-2-methyl-1,2-pentadiene (59). However, these skeletal rearrangements take place when the dienes are in contact with the above catalyst in the absence of butadiene and in the presence of a small amount of propylene. To what extent these reactions take place under the dimerization condition in the presence of excess butadiene is not known, but it is not expected to be significant.

IV

Co AND Fe CATALYST SYSTEM

A. Background

Another class of catalysts for the codimerization of ethylene and butadiene is represented by the Co- and Fe-based systems. They are grouped together because their general catalytic properties are very much alike. Co complexes and, to a lesser extent, Fe complexes have been known to be effective for butadiene oligomerization (60-64) and polymerization. Hata, Iwamoto, and co-workers (65-68) found that they are also very effective as catalysts for 1,4-hexadiene synthesis in the presence of suitable phosphines and Lewis acid or organometallic cocatalysts. Unlike the Ni or Rh counterparts, they catalyze the 1:1 codimerization to form *cis*-1,4-hexadiene instead of a *trans*-*cis* mixture. Testing of the catalyst systems to optimize their selectivity and activity has been carried out by a number of workers (69-74). Apparently, it is possible to "fine-tune" the catalyst systems by modifying the catalyst centers, the ligands, and the cocatalyst to produce an extremely selective and efficient catalyst system for *cis*-1,4-hexadiene synthesis. Attempts to produce *trans*-1,4-hexadiene with the same degree of selectivity and efficiency have so far been unsuccessful. Typical catalytic reactions demonstrating the high degree of selectivity are shown in Table XIV.

Both the Co and the Fe systems have very similar chemistry for the 1:1 codimerization reaction. Although they are almost identical in catalytic selectivity, they do differ in other catalytic properties, especially the rate of reaction (66). In practice, the Co system is superior to the Fe system; our discussion will therefore focus mainly on the former system.

TABLE XIV
COMPARISON OF CATALYTIC PROPERTIES OF SOME Fe AND Co CATALYST SYSTEMS

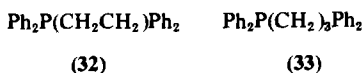
	Reference	Selectivity (%)	Rate (kg mole ⁻¹ hour ⁻¹)
Fe(AA) ₃ + Et ₃ Al	(66)	<50	3.5 (30°C)
FeCl ₃ + 2[Ph ₂ P(CH ₂) ₂ PPh ₂] + Et ₃ Al	(66)	>95	20 (80°C)
CoCl ₂ + Ph ₃ P	(66)	~10	3 (80°C)
CoCl ₂ + 2[Ph ₂ P(CH ₂) ₂ PPh ₂] + Et ₃ Al	(66)	>95	200 (80°C)
H[Co(Ph ₂ P(CH ₂) ₂ PPh ₂) ₂] + <i>i</i> -BuAlCl ₂	(69)	>95	200 (80°C)

B. Structural Feature of the Most Active Species

In the literature there are many reports of the formation of active catalyst for the 1:1 codimerization or synthesis of 1,4-hexadiene employing a large variety of Co or Fe salts, in conjunction with different kinds of ligands and organometallic cocatalysts. There must have been many structures, all of which are active for the codimerization reaction to one degree or another. The scope of the catalyst compositions claimed to be active as the codimerization catalysts is shown in Table XV (69–82). As with the nickel catalyst system discussed earlier, the preferred Co or Fe catalyst system requires the presence of phosphine ligands and an alkylaluminum cocatalyst. The catalytic property can be optimized by structural control of these two components.

1. The Phosphine Ligands

The best phosphines found so far are bisphosphines of the general formula $R_2P(CH_2)_nPR_2$, where $n = 2$ or 3 and $R =$ aryl groups. Examples of some very good ligands are 1,2-bis(diphenylphosphino)ethane (32) and 1,2-bis(diphenylphosphino)propane (33):



The activity and selectivity are significantly reduced when $n = 1$ or when $R =$ alkyl groups (83). The strong chelating effect is important and can best be demonstrated by the fact that catalysts containing the trans isomer of $\text{Ph}_2\text{P}-\text{CH}=\text{CHPPh}_2$ are significantly less efficient and selective than those containing the cis counterpart (66). It has also been found that the allylphosphine $\text{Ph}_2\text{P}-\text{CH}_2-\text{CH}=\text{CH}_2$ is almost as effective as the bisphosphine 32 for promoting the selectivity, even though the monodentate ligands, Ph_2PR , are very ineffective (70).

Tridentate phosphines (71) such as 34 as well as some nonphosphorus chelating ligands such as the bisarsines (73)



have been found to approach that of 32 or 33 in effectiveness as ligands in the Co catalyst system.

2. The Cocatalyst

The best cocatalysts are those derived from organoaluminum or organoaluminum chlorides. Certain organometallic complexes, e.g., RMgBr

TABLE XV
LIST OF COMPONENTS OF Fe AND Co CATALYST SYSTEMS: $\text{MX}_n +$
LIGAND + COCATALYST^a

X^-	Ligand ^b	Organometallic cocatalysts
Halides	R_3P	R_3Al
SCN^-	$\text{R}_2\text{P}(\text{CH}_2)_n\text{PR}_2$ ($n = 2,3$)	R_2AlCl
CO_3^{2-}	$\text{R}_2\text{PCH}_2\text{—CH=CH}_2$	RAlCl_2
SO_4^{2-}	$\text{RP}(\text{CH}_2\text{—CH=CH}_2)_2$	$\text{R}_2\text{Al}(\text{OR})_{3-x}$
RC=O—O^-	$\text{R}_2\text{P}(\text{CH}_2)_n\text{SR}$	RMgX
NO_3	$\text{P}(\text{OR})_n\text{X}_{3-n}$ ($\text{X} = \text{halides}$)	$\text{R}_4\text{Al}_2\text{SO}_4$
$\begin{array}{c} \text{O} \\ \\ (\text{CH}_3\text{—C})_2\text{CH}_2 \end{array}$	$\begin{array}{c} \text{R}_2\text{P}(\text{CH}_2)_2\text{P R}_2 \\ \quad \\ \text{O} \quad \text{O} \end{array}$	$\begin{array}{c} \text{R}_4\text{Al}^+ \text{M}^- \\ (\text{M} = \text{Li, Na, K}) \end{array}$
H^-	$\begin{array}{l} (\text{R}_2\text{PCH}_2)_3\text{CH} \\ \text{R}_3\text{As} \\ \text{R}_2\text{As}(\text{CH}_2)_n\text{AsR}_2 \\ \text{R}_3\text{Sb} \\ \text{R}_2\text{Sb}(\text{CH}_2)_n\text{SbR}_2 \end{array}$	

^a See Refs. 69–82.

^b R = Alkyl or aryl.

(83), are also effective but less desirable. As with nickel catalyst systems, these organoaluminum compounds serve the dual function of being reducing agents (if needed) and complexing agents. The choice of organoaluminum compounds depends on the initial transition metal salt used and sometimes also on the solvents (75). For example, if one starts with $\text{Co}(\text{AA})_3$ ($\text{AA} = \text{acetyl acetonate}$), the cocatalyst must be an organoaluminum chloride, R_2AlCl or RAlCl_2 , or one must work in the presence of a chloride-containing solvent. If one starts with CoCl_2 , then a nonhalide-containing cocatalyst such as R_3Al can be used. These results clearly point to the favorable effect of the presence of chloride or chlorides in the catalyst complex. Organoaluminum bromides or iodides have been tested with inferior results compared to the corresponding chlorides (83). Some examples of the influence of cocatalyst on the reactivity are shown in Table XVI in which a nonchloride-containing Co complex, $\text{Co}(\text{AA})_3$, is used in conjunction with various alkylaluminum species.

3. Postulated Catalyst Complex

From the important effects of the phosphine ligand and the organoaluminum on the catalytic properties, it is not too difficult to envision a

TABLE XVI
COMPARISON OF COCATALYST EFFECT ON THE CATALYST SYSTEMS^{a,b} Co(AA)₂-
BISPHOSPHINES-Al_xCl_{3-x}

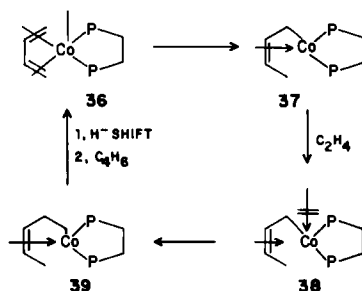
Alkylaluminum	Reaction temp. (°C)	Reaction time (hours)	Products ^c (g)			Higher- boiling residue
			1,4-HD	2,4-HD	C ₈	
(C ₂ H ₅) ₃ Al	90	2	7.9	1.05	—	0.5
(C ₂ H ₅) ₂ AlCl	85	1	60	4.8	2.1	9.5
(C ₂ H ₅) ₃ Al ₂ Cl ₃	100	1	9.2	2.7	2.5	21.4
C ₂ H ₅ AlCl ₂	100	1	30.2	5.9	4.4	9.0

^a Data from Miyake *et al.* (66).

^b Reaction conditions: toluene 50 ml, butadiene 70 ml, Co(acac)₃ 1 mmole, aluminum compound 8 mmoles, ethylene 50 kg/cm².

^c HD = Hexadiene.

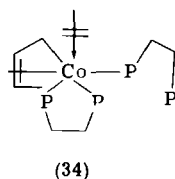
catalyst complex consisting of a lower-valent metal, a bisphosphine, and an organoaluminum chloride. The structural relationships between the transition metal catalyst center and the cocatalyst are not clear. They may be connected to each other via chloride bridges or simply associated with each other as charged complexes. It is conceivable that both these forms might exist at one time or another during the catalytic reaction. Miyake and Hata postulated a catalytic cycle (Scheme 9) which invokes a Co-hydride complex containing one molecule of the chelating phosphine **32**. Such a complex is more or less supported by the work of Harder (69) and Iwamoto (72). They found that the monovalent cobalt hydride complex $\text{HCo} \cdot 2[\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2]$, when in the presence of RAlCl_2 as cocatalyst, is as efficient and selective as the best catalyst system {e.g., $\text{CoCl}_2 \cdot 2[\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2] \cdot \text{R}_2\text{AlCl}$ } derived by other



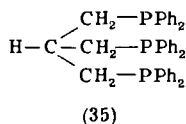
SCHEME 9. Addition of ethylene to butadiene by Co catalyst.

means. It is interesting to note that there is no obvious mechanism by which the valence of the above hydride complex can be changed under the catalytic reaction condition. This seems to support the notion that the active catalyst might have a valence of one.

The number of phosphine ligands on the active catalyst system is also subject to speculation. In Scheme 9 Hata postulated an active complex consists of only one chelating phosphine. However, he (66) and others (70, 71, 83) also observed that 2 moles of the bisphosphine **32** per mole of Co are needed for best selectivity. Sarafidis (83) suggested that a more desired structure might consist of two bisphosphines, with one of the Co—P bonds having the ability to dissociate to provide coordination sites for incoming monomers (see structure **34**).



To demonstrate his point, Sarafidis has shown that the catalyst system containing trisphosphine (71) **35** as ligand is just as effective as the one containing two bisphosphines.



Chances are, as long as there are two strong Co—P bonds existing at all times, that the requirements for selectivity will be satisfied. The use of two bisphosphines (**32**) or one trisphosphine (**35**) is merely to assure the presence of these two Co—P bonds. Thus, with a very good chelating ligand such as the bis(diphenylphosphino)propane **33**, Hata (66) showed that only a 1:1 Co/ligand ratio was needed for best selectivity.

C. Speculation on the Reaction Mechanism and Reasons for Selectivity toward *cis*-1,4-Hexadiene

The dimerization mechanism for either the Co or the Fe catalyst system is depicted in Scheme 9 according to the postulation by Hata (65) and Miyake *et al.* (66). The reaction sequences involve 1,4-addition of the

metal hydride to a cisoid-coordinated butadiene to form a butenyl complex (37) which then interacts with a coordinated ethylene to form a hexyl complex (39). A β -hydrogen elimination gives rise to the 1,4-hexadiene and regenerates the metal hydride (36).

Notice that this mechanism does not invoke the formation of a π -crotyl intermediate, as was the case with the Rh and Ni catalyst systems. The absence of the 1,2-addition product, 3-methyl-1,4-pentadiene, which would arise if a π -crotyl intermediate is present, seems to negate the presence of this species. The selectivity toward the 1,1-addition product can be explained in terms of the limited number of coordination sites on the Co atom to accommodate two C_4 olefins at the same time. This is possible as a result of efficient blockade by the chelating ligand(s). In the absence of the ligand or when the ligands are monophosphines (84), the catalyst becomes more of a butadiene oligomerization catalyst. It can be shown that under the dimerization condition, the catalyst system, $CoCl_2 \cdot 2[Ph_2P(CH_2)_2PPh_2] \cdot R_3Al$, does not catalyze the formation of polybutadiene when reacted alone with butadiene (68), nor does it catalyze the oligomerization of ethylene (67). However, at 150°C it does catalyze the oligomerization of ethylene (67).

The extreme stereoselectivity toward the synthesis of *cis*-1,4-hexadiene is attributed to the fact that only cisoid-coordinated 1,3-diene can undergo the addition reaction (65, 66). 1,3-Dienes whose cisoid conformations are sterically unfavorable do not react with ethylene under the dimerization conditions. For example, Hata (65) was able to show that, using an Fe-based catalyst system, 1-*trans*-3-pentadiene (40) and 2-methyl-1-*trans*-3-pentadiene (41) reacted readily with ethylene to form the expected 1:1 addition products, while 1-*cis*-3-pentadiene (42) and 4-methyl-1,3-pentadiene (43) failed to interact with ethylene. The explanation is that the cisoid conformations of 40 and 41 are sterically favorable while those for 42 and 43 are not.

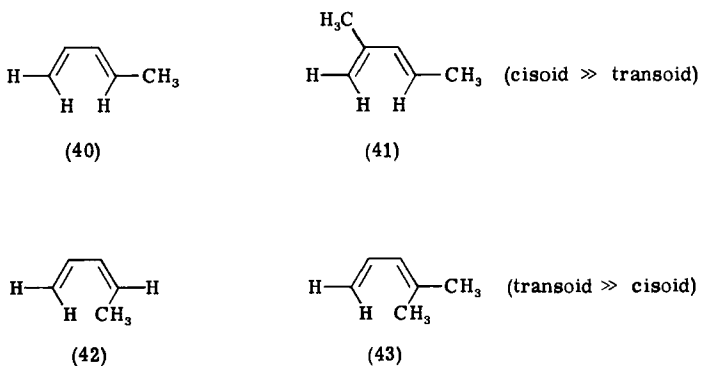


TABLE XVII
COMPARISON OF Rh-, Ni-, AND Co-BASED CATALYST SYSTEMS^a

Catalyst	Rate (g C ₄ H ₆ reacted/mole ⁻¹ hour ⁻¹)	Selectivity (1,4-hexadiene)
RhCl ₃ (H ₂ O) ₃ + HCl	436	63% at 63% BD ^b conversion
Ni(COD) ₂ + Ph ₃ P + RAlCl ₂	133	56% at 83% BD conversion
CoCl ₂ [Ph ₂ P(CH ₂) ₂ PPh ₂] ₂ + R ₂ AlCl	780	100% at 76% BD conversion ^c

^a Reaction conditions: transition metal = 1 mM, reaction time = 60 minutes at their optimum reaction condition.

^b BD = Butadiene.

^c Data provided by Sarafidis (83) extrapolated from 10 minutes' reaction time.

D. Comparison of Catalytic Property with Rh and Ni Systems

The Co system is more reactive as well as much more selective than the Ni and Rh catalyst systems (Table XVII). The best systems allow almost 100% conversion with almost 100% yield of *cis*-1,4-hexadiene. The best of the Ni and Rh systems known so far are still far from such amazing selectivity. The tremendous difference between the Ni system and the Co or Fe system must be linked to the difference in the nature of the coordination structures of the complexes, i.e., hexacoordinated (octahedral complexes) in the case of Co and Fe and tetra- or penta-coordinated (square planar or square pyramidal) complexes in the case of Ni. The larger number of coordination sites allows the Co and Fe complex to utilize chelating phosphines which are more effective than monodentate phosphines for controlling the selectivity discussed here. These same ligands are poison for the Ni (and Rh) catalyst system, as shown earlier.

V

Pd-BASED CATALYST SYSTEM

The results on Pd complexes as catalyst for the 1:1 codimerization are very limited at this time (85–87). Schneider (85, 86) found that palladous chloride in conjunction with dibutylaluminum chloride catalyzes the formation of exclusively *trans*-1,4-hexadiene as the 1:1 codimerization product of ethylene and butadiene. A *syn*- π -crotylpalladium complex was postulated as the key intermediate. The criterion for selectivity toward

the trans isomer was based on steric considerations which favored the coordinated *syn*-crotyl species over the *anti*-crotyl species.

Although Pd-based catalyst systems form only the desirable *trans*-1,4-hexadiene, their industrial value is very doubtful because of the reported poor yield of the C₆ diene and the very low activity of the dimerization reactions compared to other catalyst systems.

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Hydrogenation Reactions Catalyzed by Transition Metal Complexes

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I

INTRODUCTION

It has been some five years since my text on homogeneous hydrogenation was published in English (*1*). The book was an attempt at a comprehensive review covering the literature through 1971 and part of 1972. It was clear then that rapidly developing areas included asymmetric hydrogenation and the heterogenizing of homogeneous catalysts (or supported transition metal complexes as catalysts), and Sections III and IV

of the present review will summarize the major advances in these areas. Studies involving comparisons of homogeneous and heterogeneous catalyst have intensified, partly as a result of developments in the supported catalyst area, but mainly because of greater interest in metal clusters and their potential as catalysts. These discrete molecular species (see Section VI) can clearly provide a potential bridge between the heterogeneous multimetal-site systems and the homogeneous, usually single-site, systems.

Somewhat of a resurgence of interest in hydrogenation catalysts has resulted since the arrival of the energy crisis. A partial solution will undoubtedly involve a greater utilization of coal for the production of gaseous and liquid fuels and of petrochemicals. The conversion of coal to synthesis gas (CO and H_2), and the subsequent reduction of the carbon monoxide by hydrogen to methane, alcohols, and hydrocarbons, are processes known to be catalyzed heterogeneously but they are not generally economical. In principle, homogeneous catalysts seem attractive (see Section VI,B, and Chapter 2 by Masters in this volume).

The energy crisis has also contributed to an upsurge in the study of fundamental photochemistry of metal complexes in that a goal of many scientists is to convert sunlight into easily usable electrical or chemical energy. One aim, for example, is a chemical photosynthesis, i.e. a light-induced splitting of water molecules to make hydrogen and oxygen. This, is of course, a dehydrogenation. Catalysis of the reverse nonphotochemical reaction, hydrogenolysis of oxygen to water, is known but not well understood, although it must involve intermediate hydrides (2, 3). Photochemical studies on transition metal hydrides have appeared recently, and these have led to several new photoassisted catalytic hydrogenations. Formation of an active catalyst by photoassisted ligand expulsion from a coordinatively saturated complex is becoming increasingly well documented (see Section VIII).

Other advances over the past few years have been the development of (a) homogeneous hydrogenation catalysts for substrates normally not readily reduced, e.g., aromatics, isonitriles, and nitro compounds, and (b) a number of catalyst systems with unusual selectivity properties, e.g., with the capability of reducing α,β -unsaturated aldehydes to the corresponding α,β -unsaturated alcohols (see Sections II,B,2 and VII).

Some significant findings concerning the mechanistic details of "well-established" hydrogenation pathways (e.g., the insertion and reductive-elimination steps) have been published (see Section II), while at the other end of the scale in terms of characterized systems, the enzymatic hydrogenase system is beginning to draw attention (see Section IX). The well-established systems are reviewed first, as new systems are often compared to them in terms of reactivity and mechanism.

The number of really "new" hydrogenation catalysts, following the proliferation during the 1960's, is relatively small. This review is not a comprehensive critical one covering the recent literature, but is an attempt to discuss what I consider to be the more significant advances in the area since 1971. However, parts of the review are more of a simple cataloging of reported systems.

Some general reviews on hydrogenation using transition metal complexes that have appeared within the last five years are listed (4-7), as well as general reviews on asymmetric hydrogenation (8-10) and some dealing specifically with chiral rhodium-phosphine catalysts (11-13). The topic of catalysis by supported transition metal complexes has also been well reviewed (6, 14-29), and reviews on molecular metal cluster systems, that include aspects of catalytic hydrogenations, have appeared (30-34).

Two books (35, 36), sections in books (37-39), and reviews (40, 41) have been aimed at presenting to practicing organic chemists the principles and applications of transition metal complexes as hydrogenation catalysts. The series by Fieser and Fieser (42) is useful for tracing applications of such catalysts in organic syntheses. Several new "inorganic" texts incorporate sections or chapters devoted to metal complex hydrogenation catalysts (43-48). Some of the Specialist Periodical Reports (49-51) and the Annual Reports (52-55) of The Chemical Society, as well as the MTP series (56, 57), remain useful for keeping abreast of advances in the field.

The closely related topics of hydroformylation (58-65) and hydrogen exchange reactions (66-68) are not covered in this chapter.

II

RECENT STUDIES OF CATALYST SYSTEMS DISCOVERED PRIOR TO 1971

Background information on the initial discovery and uses of the catalysts discussed in this section are to be found in Reference 1.

A. The $RhXP_3$ and $HRuXP_3$ Catalysts¹

Mechanistic details for hydrogenation of ethylene and cyclohexene catalyzed by the well-known Wilkinson catalyst, $RhCl(PPh_3)_3$ (1, p. 204) have been further elucidated (69-74) (Fig. 1). Studies on the analogous

¹ P = tertiary phosphine-type ligand, X = monoanion.

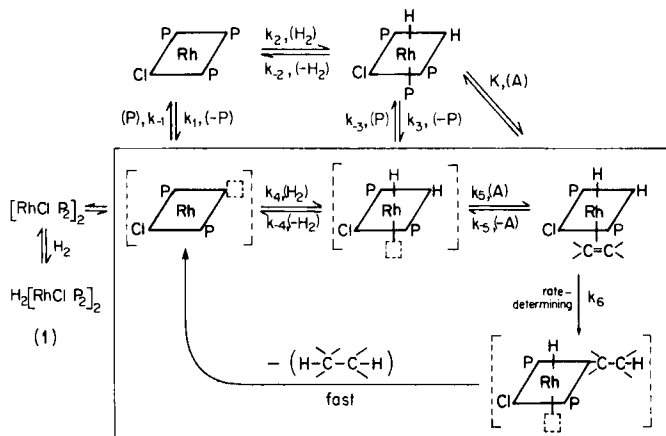
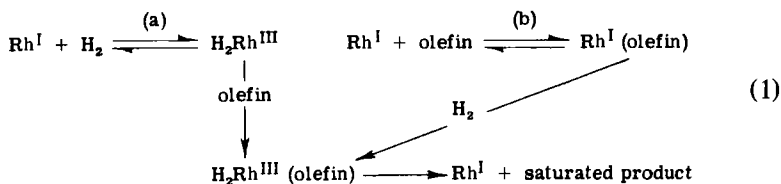


FIG. 1. Mechanistic scheme for hydrogenation of cyclohexene (A) catalyzed by $\text{RhCl}(\text{PPh}_3)_3$ in benzene ($\text{P} = \text{PPh}_3$); the major catalytic pathway is shown in the rectangle (72).

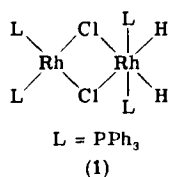
tris(*p*-tolyl) system, which involves more soluble complexes, were emphasized by the DuPont group (70). The key intermediate, $\text{H}_2\text{RhClL}_2(\text{olefin})$, where $\text{L} = \text{PPh}_3$ or presumably $\text{P}(p\text{-tolyl})_3$, is formed by initial oxidative addition of H_2 to the bis- or trisphosphine species RhClL_n , followed by reaction with olefin. These so-called "hydride" routes [Eq. 1(a)] are generally much more efficient than the so-called "unsaturate" routes in which oxidative addition of H_2 to a preformed olefin complex occurs [Eq. 1(b)]. The most effective hydride route is via the solvated RhClL_2 species, although others have concluded otherwise (71).



The hydrogens within the octahedral olefin-dihydride intermediate are transferred consecutively with overall *cis* addition, and the rate-determining step (k_6) is olefin insertion to give the alkyl-hydride. Kinetic and thermodynamic parameters for nearly all the steps of Fig. 1 have been estimated for the cyclohexene system. Because the insertion reaction is generally believed to require a *cis* disposition of the hydride and olefin

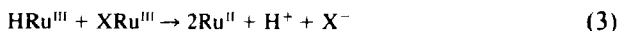
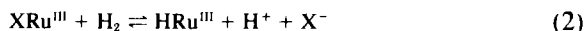
ligands (75), the k_6 path must presumably involve a cis-trans isomerization at some stage in order to yield the species with cis-disposed alkyl and hydride ligands. A number of attempts to computer-fit extensive data on cyclohexene hydrogenation to an assumed mechanism, but not usually incorporating all possible pathways, have appeared (76-78). The $\text{RhCl}(\text{PPh}_3)_3$ systems are more complex in chlorinated solvents because of formation of $\text{HRhCl}_2(\text{PPh}_3)_2$ (79).

The dimeric complex $[\text{RhClL}_2]_2$, present in varying amounts according to the conditions, is also an effective catalyst via a similar hydride route involving complex 1. An originally proposed (80) dimeric tetrahydride was not detected. Detailed crystal structures of both the red and orange forms of $\text{RhCl}(\text{PPh}_3)_3$ have appeared (81).



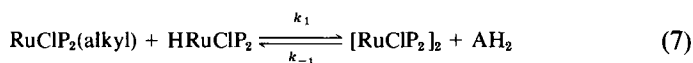
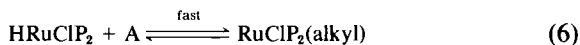
Kinetic data on cyclohexene hydrogenation catalyzed by RhClL_n species ($n = 1, 2$, or 3 ; $\text{L} = p$ -dimethylaminophenyl phosphines) were interpreted in terms of active dimer catalysts (cf. 1), possibly involving coordination through nitrogen as well as phosphorus (82).

Further mechanistic insights into hydrogenations catalyzed by $\text{HRuCl}(\text{PPh}_3)_3$ (1, p. 83) have been obtained indirectly, from studies on hydrogenation of some ruthenium(III) phosphine complexes (83). A frequently considered mechanism for hydrogen reduction of metal salts involves slow formation of an intermediate monohydride, followed by a faster reaction between the hydride and starting complex (1, p. 72), Eqs. (2) and (3):



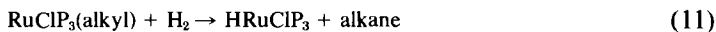
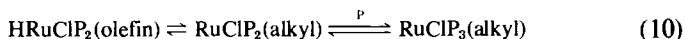
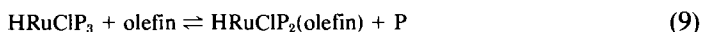
Direct evidence has now been obtained for such reactions and the intermediate hydride, using RuX_3L_2 complexes ($\text{X} = \text{Cl}, \text{Br}$; $\text{L} = \text{PPh}_3, \text{AsPh}_3$) (83). In the presence of base, the systems react further according to Eq. (4), and lead to production of bisphosphine or bisarsine complexes, the reversible reaction presumably involving a ruthenium(IV) dihydride intermediate $\text{H}_2\text{RuX}_2\text{L}_2$. The bisphosphine species (isolated as dimers) are important because of their postulated role in hydrogenation of olefins

catalyzed by $\text{HRuCl(PPh}_3)_3$ (I, p. 83). This system involves an unsaturated route, i.e., rapid reaction with olefin to give an alkyl, followed by a rate-determining reaction with H_2 to give product and regeneration of catalyst [Eq. (5)], but uncertainty exists concerning the number of coordinated phosphines [cf. Fig. 1 for the $\text{RhCl(PPh}_3)_3$ system]. Interestingly, studies of the hydrogenation of acrylamide (A) catalyzed by the bisphosphine complex in *N,N*-dimethylacetamide (DMA) reveal a quite different mechanism, as outlined below (84), where $\text{P} = \text{PPh}_3$:



Reactions such as Eq. (7), involving a metal-alkyl and metal-hydride, are well established for hydrogenations catalyzed by Co(CN)_5^{3-} (I, p. 106). The key intermediate, $[\text{RuClP}_2]_2$, is a d^7 ruthenium(I) moiety that can undergo either oxidative addition of H_2 [Eq. (8)], which is exactly analogous to hydrogen activation by Co(CN)_5^{3-} (85), or oxidative addition of C—H at an "amide-activated" sp^3 carbon (the k_{-1} step). Such C—H cleavage in aliphatic compounds at single d^8 metal centers, and to a lesser extent at d^{10} centers, to yield alkyl hydride species is known (67, 68, 86), but a two-site process, which has parallels in heterogeneous activation of alkanes (68), is attractive in terms of a search for catalysts for alkane transformations (see also Section VI). Ruthenium(I) chlorides catalyze olefin hydrogenation, but they do so via a ruthenium(III) dihydride plus olefin route (87).

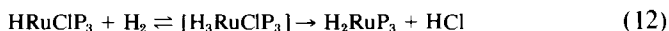
Because $\text{HRuCl(PPh}_3)_3$ does not dissociate a phosphine measurably in solution (88, 89), a plausible mechanism for catalytic hydrogenations using the trisphosphine system is now given by Eqs. (9)–(11):



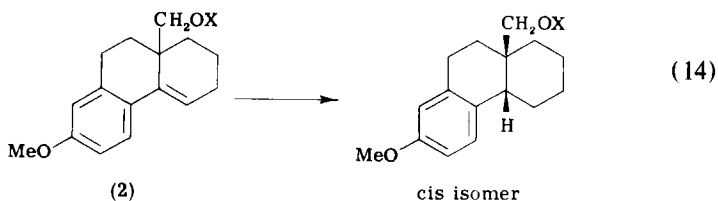
The additional phosphine ligand in the alkyl most likely favors reaction (11) (via oxidative addition) over a reaction such as (7). Stoichiometric hydrogenation of olefins can occur using $\text{HRuCl(PPh}_3)_3$ in the absence of H_2 , the second required hydrogen coming from the ortho position of a phenyl ring of the triphenylphosphine, and the ruthenium(II) product being an orthometallated complex $[(\text{PPh}_3)\text{ClRu}(\text{o-C}_6\text{H}_4\text{PPh}_2)]_2$ (88); this reaction proceeds via the trisphosphine alkyl intermediate

$\text{RuCl}(\text{PPh}_3)_3(\text{alkyl})$ (90). Because of the fact that the orthometallated complex reacts with H_2 to re-form $\text{HRuCl}(\text{PPh}_3)_2$, catalytic hydrogenation of olefins can result via such pathways, although product formation via reaction (11) is kinetically preferred (88).

Some data on D_2 - H_2 exchange using $\text{HRuCl}(\text{PPh}_3)_3$ in benzene indicate that the original $\text{Ru}-\text{H}$ bond is not involved, and it has been suggested (91) that olefin hydrogenation catalyzed by this complex may proceed via $\text{H}_2\text{Ru}(\text{PPh}_3)_3$ or $\text{H}_4\text{Ru}(\text{PPh}_3)_3$ species formed according to Eqs. (12) and (13) [cf. Eq. (4)]:



The $\text{RhCl}(\text{PPh}_3)_3$ and $\text{HRuCl}(\text{PPh}_3)_3$ [or the precursor $\text{RuCl}_2(\text{PPh}_3)_3$] complexes continue to be widely used in organic syntheses generally [see James (1), pp. 83 and 204], for a variety of catalytic reactions. The volumes by Fieser and Fieser (42) list such applications thus far to early 1974, and for hydrogenation, besides those discussed elsewhere in this Chapter, these include for the rhodium system selective reduction of olefinic bonds within steroids (92), terpenes (93), prostaglandins (94), and allenes (95). Intramolecular coordination of the polar group is envisaged in the hydrogenation of 2 catalyzed by $\text{RhCl}(\text{PPh}_3)_3$, because reaction (14) takes place with $\text{X} = \text{alkali metal ion}$ but not with $\text{X} = \text{H}$ (96).

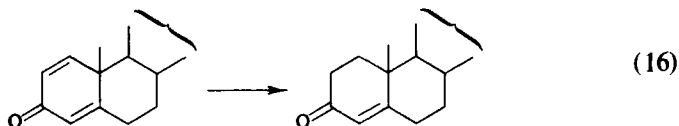


2-Butyne-1,4-diol has been hydrogenated to the 2-butene-diol (97), mesityl oxide to methylisobutylketone (98), and epoxides to alcohols (98a). The rhodium complex and a related solvated complex, $\text{RhCl}(\text{solvent})(\text{dppb})$, where $\text{dppb} = 1,4\text{-bis}(\text{diphenylphosphino})\text{butane}$, have been used to hydrogenate the ketone group in pyruvates to give lactates (99) [Eq. (15)], and *in situ* catalysts formed from rhodium(I) precursors with phosphines can also catalyze the hydrogenation of the imine bond in Schiff bases (100) (see also Section III,A,3).

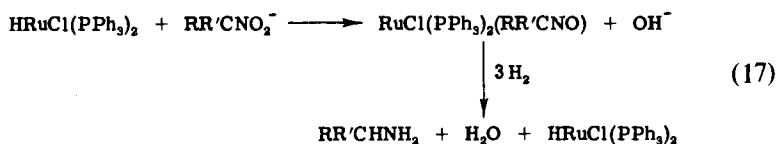


The $\text{RuCl}_2(\text{PPh}_3)_3$ complex has now been used to selectively hydrogenate 1,5,9-cyclooctatriene to the monoene (101), dienes to monoenes

(101), and saturated aldehydes (even in aldehyde/ketone mixtures) to the alcohols (102). The $\text{RuCl}_2[(p\text{-XC}_6\text{H}_4)_3\text{P}]_3$ complexes, especially in the presence of a base such as triethylamine, hydrogenate 1,4-androstadiene-3,17-dione selectively to the 4-ene in a reaction which is first-order in steroid concentration; reactivity decreases in the order $\text{X} = \text{OMe} > \text{Me} > \text{H}$ (103, 103a):

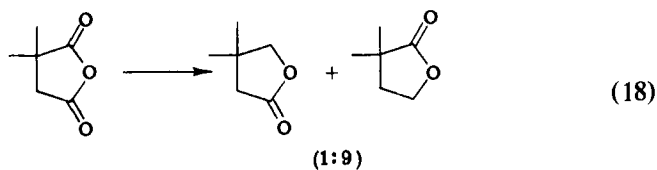


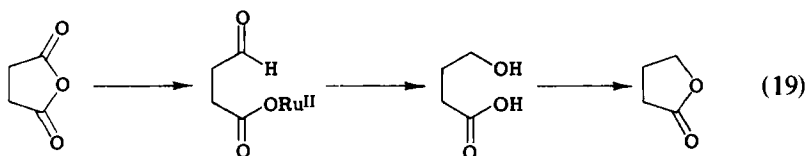
$\text{RuCl}_2(\text{PPh}_3)_3$ in the presence of base also seems useful for catalytic hydrogenation of aliphatic and aromatic nitro compounds to the amines (120°C, 90 atm H_2) (104, 105); for example, addition of hydroxide converts a nitroalkane to the anionic form $\text{RR}'\text{C NO}_2^-$, and a suggested hydrogenation route is shown in Eq. (17), although hydrogenation of $\text{HRuCl}(\text{PPh}_3)_2(\text{PhNO}_2)$ intermediates was favored for nitrobenzene reduction (104):



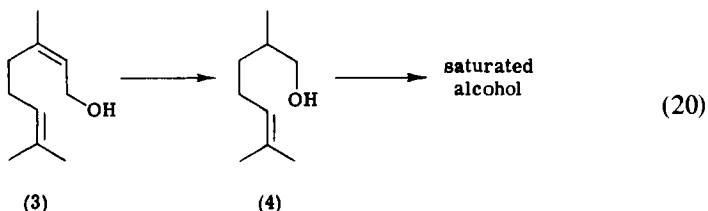
High selectivity is observed, and in aromatic compounds other substituents (CO_2R , OR, CN, halide) are not affected. Dinitro aromatics could be sequentially hydrogenated to nitroamines and diamines (105). [Some ruthenium and iron carbonyls were less effective (104)].

Selective hydrogenation (10 atm) of cyclic carboxylic acid anhydrides to γ -lactones has also been accomplished using $\text{RuCl}_2(\text{PPh}_3)_3$ (106, 107). Unsymmetrically substituted anhydrides give lactones in which the least-hindered carbonyl is reduced [Eq. (18)], in contrast to LiAlH_4 reductions. Initial cleavage of the $\text{C}-\text{O}$ bond by the ruthenium(II) hydride, followed by catalytic hydrogenation of the carbonyl, constituted a reasonable mechanism (106):

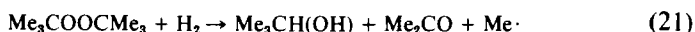




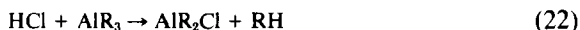
Both the rhodium and ruthenium catalysts have been used to successively hydrogenate the terpene geraniol (3) to citronellol (4) and 3,7-dimethyloctanol (108):



Further work on deuteration of cycloalkenes catalyzed by $\text{RhCl}(\text{PPh}_3)_3$ has appeared (109), as have more initial rate data for hydrogenation of olefinic substrates using $\text{RhCl}(\text{PPh}_3)_3$ (110–112) and $\text{HRuCl}(\text{PPh}_3)_3$ (113) in a range of solvents, in both the presence and absence of oxygen. More details have appeared on the nature of oxygenated and oxidized rhodium(I) triphenylphosphine complexes (114–118) and their use as hydrogenation catalysts (98, 115, 119, 120), and in this regard it should be noted that both $\text{RhCl}(\text{PPh}_3)_3$ and $\text{RuCl}_2(\text{PPh}_3)_3$ catalyze the decomposition of peroxides by H_2 (121):



Addition of aluminum alkyls enhances the reactivity of $\text{RuCl}_2(\text{PPh}_3)_3/\text{H}_2$ -catalyzed systems primarily by scavenging HCl according to reaction (22), and this promotes hydride formation, cf. Eq. (4) (122, 123).



Ruthenium alkyls were also formed via chlorine-alkyl interchange. An enhancement of the activity of $\text{RhCl}(\text{PPh}_3)_3$ by AlBr_3 was simply due to formation of the more active bromo complex, while enhancement by addition of $\text{Al}(\text{i-Bu})_3$ was attributed to formation of $\text{HRh}(\text{PPh}_3)_3$ (see Section II,B,1).

Besides the known activity of $\text{HRuX}(\text{PPh}_3)_3$ complexes where X is a carboxylate (1, p. 85), other complexes with X an α -hydroxycarboxylate and related bridged dimers $[\text{HRu}(\text{PPh}_3)_3]_2\text{X}$ have been found to effect alkene hydrogenation (124).

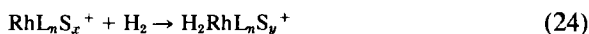
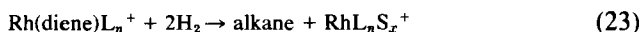
Use of diphenylphosphinobenzene-*m*-sulfonic acid (DPM) allows for-

mation of water-soluble complexes of ruthenium(II) and rhodium(I). The HRuX(DPM)_3 systems ($\text{X} = \text{Cl}$ or acetate) catalyze under mild conditions hydrogenation of unsaturated carboxylic acids, and β -ketoacids to the alcohols, the hydrogenation rates being pH-dependent (125, 126). The ketone group in fructose and 1,3-dihydroxyacetone were also hydrogenated, and the triphenylphosphine system $\text{HRuCl(PPh}_3)_3$ in DMA has also been noted to hydrogenate these substrates as well as other aldoses and ketoses. Accompanying decarbonylation, for example, of the sugar aldehyde group, was inhibited by hydrochloric acid, present from the *in situ* preparation of the hydride from $\text{RuCl}_2(\text{PPh}_3)_3$ (127). An uncharacterized rhodium-DPM complex in water was reduced by H_2 to metal (125). Some water-soluble hydroxymethylphosphine complexes of rhodium(I) and rhodium(III), as well as palladium(II) and platinum(II), are not active for hydrogenation in water, although the rhodium(I) systems show some activity in benzene or ethanol (128). Water-soluble catalysts are potentially useful in phase-transfer catalysis (see Section V).

B. Other Rhodium and Ruthenium Catalysts

1. Containing Tertiary Phosphine-Type Ligands

The cationic complexes Rh(diene)L_2^+ (L is a tertiary phosphine, phosphite, or arsine) were reported by several groups in 1969-1970 (1, p. 270), but Osborn *et al.* (129-132) first reported on their potential for hydrogenation of olefins, acetylenes, and ketones. Full details on these systems have now appeared (133-135), and the important equilibria governing the active catalysts are given in Eqs. (23)-(25). An important difference from



(5)

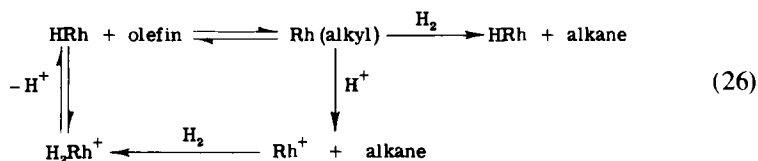


(6)

$n = 2$ or 3 ; x , y , and z unknown; S = solvent acetonitrile, 2-butanone, DMA, acetone, alcohol

the related Wilkinson-type systems where a rhodium(III) dihydride prevails (see Fig. 1) is the presence of the rhodium(I) monohydride catalyst governed by equilibrium (25); this is sensitive to the nature of L and S and can be shifted by addition of acid or base to give solutions containing

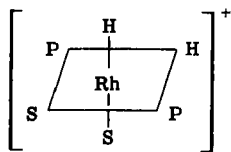
the dihydride (**5**) or monohydride (**6**), respectively. The neutral monohydride **6** is a powerful hydrogenation catalyst for simple olefins, as well as an isomerization catalyst in the familiar reversible hydrometallation mechanism (133). The hydrogenation mechanism via **6** was not elucidated; hydrogenolysis of an intermediate alkyl as established, for example, for $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ (1, p. 250), or protonolysis of the alkyl (1, p. 402), could complete the catalytic cycle:



The dihydride **5** is a moderately active olefin hydrogenation catalyst via a hydride route [Eq. 1(a)], and does not give rise to concomitant isomerization (133). Unsaturate routes via reaction of H_2 with cationic olefin complexes were unimportant, at least for weakly coordinating olefins (133). More strongly coordinated dienes were hydrogenated specifically to monoolefins via such a route, in which $\text{Rh}(\text{diene})\text{L}_2^+$ is the only detectable species; bidentate phosphine or arsine ligands were most effective because they prevented formation of inactive $\text{Rh}(\text{diene})_2\text{L}^+$ species (135). Conditions were also found for extremely selective reduction of acetylenes, including 2-hexyne to *cis*-2-hexene, and 1-hexyne to 1-hexene, using **5** or **6** with monodentate ligands (134).

The likely dihydride-diene intermediates in a reaction such as (23) have been detected for some corresponding cationic iridium complexes (136-138) (see Section II,C). Of interest here, the complex $\text{Rh}(\text{NBD})(\text{diphos})^+$, where NBD = norbornadiene and diphos = 1,2-bis(diphenylphosphino)ethane, is found to absorb in methanol only 2 moles of H_2 per rhodium with formation of norbornane (138a), whereas the corresponding PPh_3 complex reacts with 3 moles to give a cationic dihydride [Eqs. (23) and (24)]. The rhodium product is monomeric solvated $\text{Rh}(\text{diphos})^+$, but it is isolated as a binuclear $[\text{Rh}_2(\text{diphos})_2][\text{BF}_4]_2$ salt, in which each rhodium is bonded to two phosphorus atoms of a diphos and, through symmetrical π -arene coordination, to a phenyl ring of the diphos ligand of the other rhodium atom. In the presence of base, including triethylamine (a common additive in catalytic asymmetric hydrogenation systems, see Section III,A,1), the methanolic solutions contain $\text{Rh}_3(\text{diphos})_3(\text{OMe})_2^+$ which has triply bridged methoxides. The $\text{Rh}(\text{diphos})^+$ solutions effect catalytic hydrogenation, via an unsaturated route [see Eq. 1(b)], of various alkenes and derivatives, including styrenes

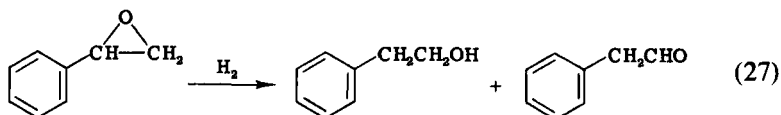
and acrylic acids which are typical substrates in asymmetric systems. Some alkene and arene binding constants are of interest [benzene ($18 M^{-1}$), toluene (97), xylenes (~ 500), 1-hexene (2), styrene (20), methyl acrylate (3)] in that they suggest that binding of styrene is primarily via the phenyl ring; $Rh(\text{diphos})(\text{benzene})^+$ was isolated as the BF_4^- salt. The different reactivities of $Rh(\text{NBD})(\text{diphos})^+$ and $Rh(\text{NBD})(PPh_3)_2^+$ toward H_2 were attributed (138a) to the fact that only the latter can form a *cis*-dihydride (5) in which neither hydride is in an unfavored position *trans* to a phosphine (133).



S = solvent, P = PPh_3

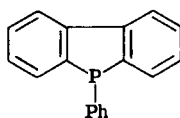
(5)

The complex $[Rh(\text{COD})L^1L^2]^+$, where $L^1 = PPh_3$ and $L^2 = \text{pyridine}$, and a neutral benzoate complex, $Rh(\text{COD})(PPh_3)(\text{OCOPh})$, also effect highly selective hydrogenation of 1-alkynes to 1-alkenes as well as reduction of 1-alkenes and ketones to alcohols (139); the one equivalent of base required may be related to monohydride formation [Eq. (25)]. The bisphosphine complexes also catalyze reduction of styrene oxide to 2-phenylethanol and phenylacetaldehyde (140):



The $Rh(\text{COD})(PPh_3)(\text{acetone})^+$ complex is a useful precursor for the mixed L^1L^2 cation complexes (140a).

Hydrogenation of 1,3-dienes to terminal olefins is catalyzed by $HRh(PPh_3)_4$ and $[Rh(\text{CO})_2(PPh_3)_2]_2$ in the presence of excess phosphine; diene insertion into a metal-hydride bond to give σ -alkenyl rather than π -allyl intermediates was postulated for the initial step (141). Mechanistic studies of the $HRh(PPh_3)_4$ catalyst (142) and a more reactive phosphole analog (143) $HRh(\text{DBP})_4$ [5-phenyl-5*H*-dibenzophosphole (DBP), 7] for

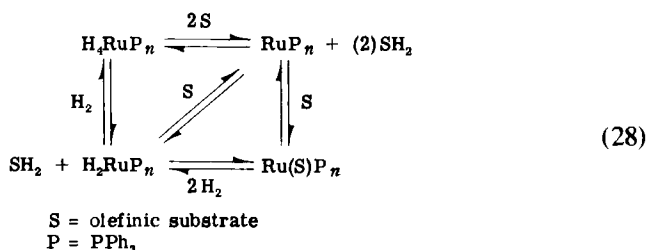


(7)

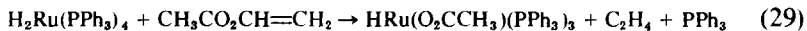
olefin hydrogenation indicate active bisphosphine species operating by the usual unsaturate route, Eq. (5).

A *cis*-RuCl₂(CO)₂(PPh₃)₂ complex, which catalyzes hydrogenation of dienes and monoenes, becomes useful in the presence of added phosphine for selective hydrogenation of 1,5,9-cyclododecatriene to cyclododecene; the catalyst is a HRuCl(CO)₂(PPh₃)₂ hydride that operates via steps analogous to those of reactions (9)–(11) (144, 145).

The H₂Ru(PPh₃)₄ and H₄Ru(PPh₃)₃ catalysts are thought to operate by pathways outlined in Eq. (28) (146):



The olefin complexes Ru(olefin)(PPh₃)₃ have been synthesized via reaction of the alkene with H₂Ru(PPh₃)₄ or H₄Ru(PPh₃)₃, presumably via hydridoalkylruthenium(II) intermediates since alkane is liberated (146, 147), but some isolated hydridoalkyls have now been shown to reductively eliminate alkane with formation of the hydrido orthometallated ruthenium(II) complex rather than the "expected" ruthenium(0) complex (148), and so a number of the olefin complexes have to be reformulated. For example, Ru(C₂H₄)(PPh₃)₃ has been shown to be $\overline{\text{HRu}(\text{O}-\text{C}_6\text{H}_4\text{PPh}_2)(\text{C}_2\text{H}_4)(\text{PPh}_3)_2}$ (149). Of further interest, the expected product from methacrylate undergoes oxidative addition of the vinylic C—H bond to yield a hydrido- σ -propenyl complex $\overline{\text{HRu}[\text{CH}=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OR}](\text{PPh}_3)_3}$ (147), while some alkenyl carboxylates react with H₂Ru(PPh₃)₄ with C—O bond cleavage to give the carboxylate complex, as shown in Eq. (29) [cf. Eq. (19)] (150):



Reaction (29) seemed general for a number of group VIII metal hydrides, including HRuCl(PPh₃)₃, HRh(PPh₃)₄, HCo(N₂)(PPh₃)₃, H₂Fe(N₂)(PPh₂Et)₃, and H₂Pd[P(C₆H₁₁)₃]₂ (150). Olefin hydrogenation catalyzed by H₂Ru(PPh₃)₄ can be inhibited by nitrogen as a result of its preferred binding over olefinic substrate and resulting formation of H₂Ru(N₂)(PPh₃)₃ (151, 152).

The cationic ruthenium(II) phosphine complexes such as solvated $\text{Ru}(\text{PPh}_3)_3^{2+}$, readily prepared by protonation of carboxylate complexes, appear to catalyze hydrogenation of mono- and diolefins by both a hydride route via $\text{H}_2\text{Ru}(\text{PPh}_3)_n^{2+}$ and an unsaturate route via $\text{Ru}(\text{alkene})(\text{PPh}_3)_n^{2+}$ (153, 154). Related rhodium catalysts result from protonation of $\text{Rh}(\text{O}_2\text{CMe})_2(\text{PPh}_3)_2$ (155), and $\text{H}_2\text{Rh}(\text{O}_2\text{CR})(\text{PPh}_3)_2$ carboxylate complexes are themselves active (156).

A review is concerned with carboxylate complexes of platinum metals and their versatility as catalysts; their moderate stability and high lability (the monodentate, bidentate character of the carboxylate ligand, and its ready removal by acid) render them particularly promising (157).

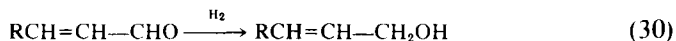
More initial rate data for monoene substrates have appeared using as catalysts $\text{RhCl}(\text{CO})\text{P}_2$, $\text{HRh}(\text{CO})\text{P}_3$ (110, 158), and $\text{Rh}(\text{NO})\text{P}_3$ (110, 157), where P is a tertiary phosphorus donor. Borohydride reduction of $\text{Rh}(\text{NO})(\text{PPh}_3)_2\text{Cl}$ gives an active catalyst (159).

A recent paper (160) summarizes studies involving stoichiometric hydrogenation of the olefinic link in unsaturated phosphines (e.g., *o*-vinylphenyl- or but-1-enyldiphenylphosphine) when coordinated at rhodium.

Rate data have appeared (161) for the hydrodimerization of acrylonitrile to adiponitrile, which is catalyzed by various ruthenium-phosphine complexes (1, p. 101).

2. Other Ligands

The very unusual selective hydrogenation of α,β -unsaturated aldehydes to the unsaturated alcohols, Eq. (30), has been accomplished using $[\text{RhCl}(\text{CO})_2]_2$ in the presence of tertiary amines under oxo conditions (162). $\text{RhCl}(\text{PPh}_3)_3$ systems under similar conditions reduce the olefinic bond (162), as do $\text{Co}_2(\text{CO})_8$ systems in the presence of amines or phosphites (163). Further details on the versatile $\text{Rh}(\text{BH}_4)(\text{amide})\text{py}_2\text{Cl}_2$ systems (1, p. 280) have appeared (164, 165); ketones are also slowly hydrogenated (166), and 1,5,9-cyclododecatriene has been selectively reduced to cyclododecene (167).

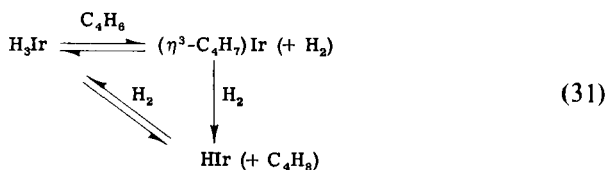


Details have now appeared on the use of chlororhodate(I), chlororuthenate(I), and rhodium(I) diethylsulfide complexes for hydrogenation of unsaturated carboxylic acids (87, 168), and on the use of bromorhodate(III) species for the hydrogen reduction of iron(III) (169). Further mechanistic details have appeared on olefin hydrogenation catalyzed by $[(\pi\text{-arene})\text{RuCl}_2]_2$ complexes, a triphenylbenzene system being the most active (170); a monomeric $(\pi\text{-arene})\text{RuH}$ species was a suggested inter-

mediate (171). The pentamethylcyclopentadienyl rhodium and iridium catalysts $[\eta^5\text{-C}_5\text{Me}_5\text{MCl}]_2(\mu\text{-H})(\mu\text{-Cl})$ have now been fully characterized; hydrogenation of monoenes at ambient conditions likely involves monomeric species operating by hydride routes (172-174).

C. Iridium and Cobalt Catalysts

Further mechanistic studies on systems using $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ favor unsaturate pathways (175, 176), while $\text{H}_3\text{Ir}(\text{CO})(\text{PPh}_3)_2$ systems involve both the trihydride and a monohydride complex which are in equilibrium (177, 178). The complexes can also effect selective hydrogenation of conjugated and unconjugated dienes to monoenes (178, 179). Reaction (31) shows a suggested scheme for butadiene hydrogenation catalyzed by the trihydride, where $\text{Ir} = \text{Ir}(\text{CO})(\text{PPh}_3)_2$ (178):

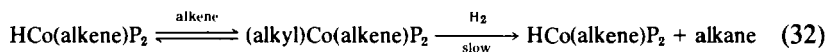


The π -allyl can also be formed directly from the monohydride. Paths involving *o*-metallated species were also invoked for ethylene hydrogenation (178) [cf. the $\text{HRuCl}(\text{PPh}_3)_3$ systems discussed in Section II,A]. Initial rates of hydrogenation for olefinic substrates in a range of solvents keep appearing for the catalysts $\text{IrCl}(\text{CO})\text{P}_2$, $\text{HIr}(\text{CO})\text{P}_3$, IrClP_3 , H_3IrP_3 , and $\text{Ir}(\text{NO})\text{P}_3$, where P is a tertiary phosphine (110, 112, 158, 159, 180). The iridium and cobalt complexes $\text{M}(\text{NO})(\text{PPh}_3)_2\text{Cl}_2$ give active catalysts after treatment with borohydride (159).

The cationic iridium complexes $\text{Ir}(\text{diene})\text{L}_2^+$ (L = phosphine-type ligand) were originally reported along with their rhodium analogs (Section II,B,1). The complexes and ones with mixed ligands, e.g., $\text{Ir}(\text{diene})(\text{PPh}_3)(\text{py})^+$, are active for hydrogenation of dienes and alkenes (136-138). Interestingly, a *cis,cis*-complex, $\text{H}_2\text{Ir}(\text{COD})(\text{Ph}_2\text{PMe})_2^+$, was detected at low temperature, giving direct evidence for an intermediate in a reaction such as (23). An isomer with *cis*-hydrides and *trans*-phosphines was later isolated (138).

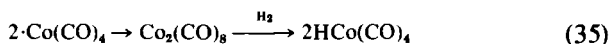
The cyclooctene dimer $[\text{IrCl}(\text{C}_8\text{H}_{14})_2]$ can selectively hydrogenate cyclooctene in mixtures with hex-1-ene, and an unsaturate route [Eq. 1(b)] via a monomeric olefin complex was demonstrated (181). The pentamethylcyclopentadienyl dimer was mentioned at the end of Section II,B,2.

Detailed mechanistic studies have appeared for the $\text{H}_3\text{Co}(\text{PPh}_3)_3$ -catalyzed hydrogenation of terminal and cyclic olefins in benzene (182-184). The catalytic cycle consists of coordination of the substrate to a solvated $\text{H}_3\text{Co}(\text{PPh}_3)_2$ intermediate with displacement of solvent, followed by transfer of two hydrogens to the substrate with formation of a monohydride; subsequent H_2 absorption regenerated the trihydride. The first hydride transfer was considered rate-determining. Thermodynamic and kinetic entropy data could be rationalized satisfactorily only if solvation was taken into account. The $\text{HCo}(\text{N}_2)(\text{PPh}_3)_3$ complex after displacement of the N_2 by substrate also effects cyclohexene hydrogenation; the hydride route mentioned above was considered, but the unsaturated route outlined in Eq. (32) was favored, in which coordination of a second alkene promotes hydrogen transfer within a monohydride complex (185):



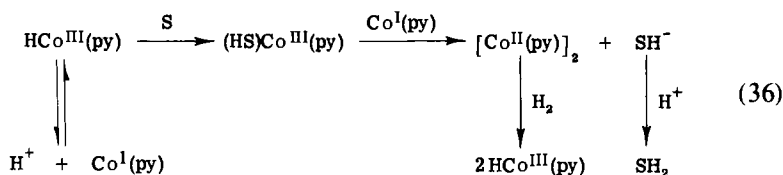
The cobalt(I) complex $\text{CoBr}(\text{PPh}_3)_3$ as a boron trifluoride etherate selectively hydrogenates conjugated dienes to monoenes via an unusual 1,2-hydrogen addition at the *more-substituted* double bond (186).

Saturated ketones and aldehydes have been reduced to alcohols using $\text{Co}_2(\text{CO})_8$ -phosphine (P) mixtures at high H_2 pressures, probably via the coordinatively unsaturated species $\text{HCo}(\text{CO})_2\text{P}$ (187). A reassessment of experimental data on hydrogenation of aromatics (A) catalyzed by $\text{Co}_2(\text{CO})_8$ under hydroformylation conditions has led to the suggestion that free radicals rather than organocobalt complexes are involved (188), e.g.,

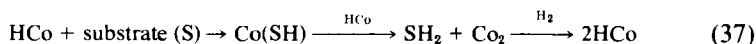


The hydrogenations become analogous to those involving $\text{HMn}(\text{CO})_5$ (see Section II,D), and to some catalyzed by $\text{HCo}(\text{CN})_5^{3-}$ (see below). Use of bis(dimethylglyoximate)cobalt(II)-base complexes or cobaloximes(II) as catalysts (1, p. 193) has been more thoroughly studied (189, 190). Alkyl intermediates have been isolated with some activated olefinic substrates using the pyridine system, and electronic and steric effects on the catalytic hydrogenation rates have been reported (189). Mechanistic studies have appeared on the use of (pyridine)cobaloxime(II) with H_2 , and of (pyridine)chlorocobaloxime(III) and vitamin B_{12} with borohydride, for reduction of α,β -unsaturated esters (190). Protonation of a carbanion

formed from an intermediate cobalt(III) alkyl was thought to give the hydrogenated product, e.g. (S = substrate),

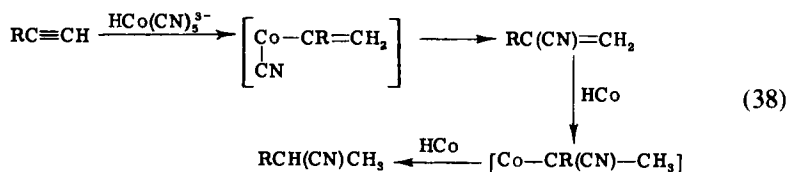


Detailed analysis of kinetic data for hydrogenation of cinnamate catalyzed by aqueous $\text{Co}(\text{CN})_5^{3-}$ (1, p. 110) supports successive hydrogen-atom transfers from $\text{Co}^{\text{II}}(\text{CN})_5(\cdot\text{H})^{3-}$ species to uncoordinated substrate [cf. Eq. (33)], rather than hydride transfer from $\text{HCo}^{\text{III}}(\text{CN})_5^{3-}$ to give a cobalt-alkyl (191, 192). *trans*-1-Phenylbuta-1,3-diene hydrogenation is thought to proceed via the same radical mechanism in glycerol-methanol, but in water the mechanism via organometallics was favored (193):



Evidence for cobalt σ -butenyl and π -methylallyl intermediates in butadiene hydrogenations has been obtained using Raman spectroscopy (194), which could be a useful probe for catalytic reactions, especially in aqueous solutions.

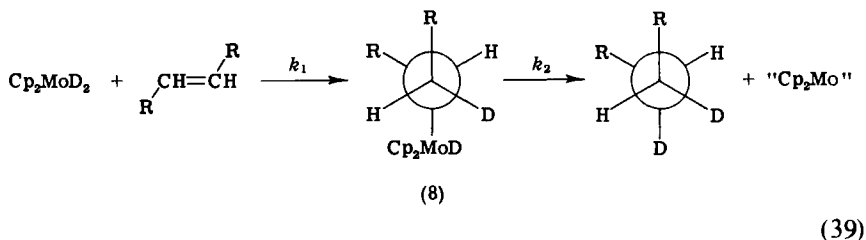
The aqueous $\text{Co}(\text{CN})_5^{2-}$ solutions under H_2 have been found to catalyze hydrogenolysis of C_4 -unsaturated alcohols to butenes but, more remarkably, with acetylenic alcohols besides hydrogenated products secondary nitriles are also formed by addition of HCN (stoichiometric with respect to cobalt) (195):



D. Other Catalysts

An important study using cyclopentadienyl (Cp) molybdenum species (196) has shown that reductive elimination of saturated product from an alkyl-hydride complex occurs with retention of configuration at the

metal-bonded carbon, Eq. (39):



The initially expected (75) *cis*-hydrometallation or olefin-insertion step with fumarate ($\text{R} = \text{CO}_2\text{Me}$) yields the *threo* isomer 8, which then undergoes the k_2 step with retention to give racemic 1,2-dideuterosuccinate. Such retention is necessary to give the usually observed (1, p. 407) overall *cis* addition of H_2 to olefinic bonds, but this study provided the first direct experimental proof, the difficulty being the scarcity of stable metal alkyl-hydride intermediates. The Cp_2MoH_2 complex also catalyzes hydrogenation of 1,3- or 1,4-dienes to monoenes (197).

The complexes $\text{Cr}(\text{CO})_3\text{L}$, with L = phenanthrene, naphthalene, or anthracene, are more active for diene hydrogenation than with L = substituted benzenes (see also Section VIII), and this is attributed to an easier displacement of the arene by the diene substrate, the phenanthrene type being asymmetrically bonded, having two longer and more readily cleaved chromium-carbon bonds (198, 199).

A further report has appeared on hydrogenation of monoenes catalyzed by $\text{Mn}_2(\text{CO})_{10}$ (200). The stoichiometric hydrogenation of α -methylstyrene by hydridopentacarbonylmanganese(I) [Eq. (40)] has been shown to proceed via a free-radical mechanism, involving hydrogen-atom transfer from the manganese [see Eqs. (33 and 34)]; the observation of CIDNP (chemically induced dynamic nuclear polarization) effects in NMR spectra, especially the polarization of the doublet signal arising from the methyl protons of the isopropylbenzene, was attributed to competition within the geminate radical pair [$\text{C}_6\text{H}_5\dot{\text{C}}(\text{CH}_3)_2$, $\text{Mn}(\text{CO})_5$] to re-form reactants or to separate into the radicals with ultimate formation of products (201).



The complex $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})(\text{PhC}\equiv\text{CPh})$ catalyzes mild hydrogenation of acetylenes, dienes, and olefins, following hydrogenation of the coordinated acetylene (202); the monocarbonyl is the likely intermediate in hydrogenation of acetylenes using $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$ (1, p. 44).

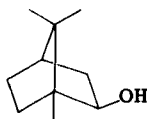
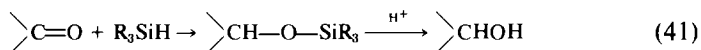
The osmium hydrides $\text{H}_4\text{Os}(\text{PEtPh}_2)_3$ and *cis*- $\text{H}_2\text{Os}(\text{PEtPh}_2)_4$ catalyze

hydrogenation of monoenes, but there is considerable accompanying isomerization (203). Hexachloroplatinic acid and stannous chloride mixtures in acetic acid and isopropanol provide homogeneous and heterogeneous catalysts, depending on the Pt:Sn ratio, for hydrogenation of olefins and acetylenes (204, 205) (see also Section VI,A).

Transition metal stearates have been shown *not* to have catalytic activity (206). The considerable literature on these systems, developed by Tulupov, has been reviewed, and the unique mechanism presented has been questioned (1, p. 384).

E. Reduction of Carbonyls and Imines via Hydrosilylation

Although there are now several catalysts useful for hydrogenation of saturated carbonyl compounds to alcohols (see Section XII), an alternative approach has involved initial hydrosilylation (Chapter 9 in this volume) followed by acid hydrolysis [Eq. (41)]. The area first developed using principally the $\text{RhCl}(\text{PPh}_3)_3$ catalyst (207–210), and has since proved particularly useful in asymmetric syntheses (see Section III,A,4). Besides simple aliphatic and aromatic aldehydes and ketones, the terpene-ketones camphor and menthone were stereoselectively reduced to mainly the less stable alcohols; e.g., camphor gave **9** (209).

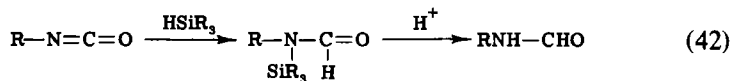


(9)

One or both carbonyls in β -diketones can be reduced, as well as the carbonyl function in acyl cyanides (210). Similar treatment of α,β -unsaturated ketones and aldehydes can lead to the saturated carbonyl products via selective reduction of the olefinic bond (207, 208, 210); see Eq. (51) in Section III,A,4. Some terpenes (α - and β -ionone, pulegone) were reduced in this way (208). Platinum(II) phosphine complexes have been used for the hydrosilylation of saturated ketones and could be used for the reduction (211).

The hydrosilylation-hydrolysis route is also effective for reduction of imines ($>\text{C}=\text{N}-$) to amines (see also Section III,A,4). The $\text{RhCl}(\text{PPh}_3)_3$

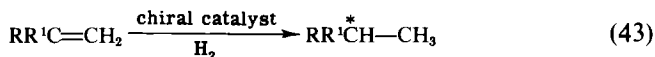
catalyst has been used in this way to reduce Schiff bases of the type $\text{PhCR}^1=\text{NR}^2$ ($\text{R}^1 = \text{H}, \text{CH}_3$; $\text{R}^2 = \text{Ph}, \text{Me}, n\text{-Bu}$); other rhodium(I) and palladium(II) catalysts were less effective (212). The imine group in isocyanates can similarly be reduced to give formamides using, for example, PdCl_2 as catalyst (213):



III

ASYMMETRIC HYDROGENATION

The subject of asymmetric synthesis generally (214, 215) gained new momentum with the potential use of transition metal complexes as catalysts. The use of a complex with chiral ligands to catalyze a synthesis asymmetrically from a prochiral substrate is advantageous in that resolution of a normally obtained racemate product may be avoided, for example,



If R and R^1 are not a methyl group, the process generates a chiral carbon center (C^*). The overall catalytic addition of hydrogen to olefinic bonds generally is nearly always *cis* (1, p. 407) and to the olefinic face coordinated to the metal. This *cis*-*endo*-addition produces a chiral center(s) when one olefinic face is preferentially coordinated.

A. Rhodium Catalysts with Chiral Phosphines

1. Olefinic Substrates

The review of Morrison *et al.* (10) traces the development of the use of rhodium-chiral phosphine catalysts to about the end of 1974. This field was initiated by the suggested incorporation (216) of chiral phosphines, instead of triphenylphosphine, into the so-called Wilkinson catalyst, $\text{RhCl}(\text{PPh}_3)_3$ (Section II,A), or into closely related systems. Horner's group (217, 218) used such catalysts, formed *in situ* in benzene from precursor $[\text{Rh}(\text{diene})\text{Cl}]_2$ complexes and MeP^*PhR phosphines ($\text{R} = n\text{-Pr}, i\text{-Pr}, n\text{-Bu}, t\text{-Bu}$) for hydrogenation of α -substituted styrenes and

obtained optical purities² up to 19%. Essentially simultaneously, Knowles *et al.* (the Monsanto group) developed the use of the "same" catalyst systems, but in alcohol-benzene media, for hydrogenation of various α,β -unsaturated acids to products with up to 28% ee² (219, 220). The hydrogenations were promoted (both rates and optical purities) by use of salts of the olefinic acids, and this was rationalized in terms of more effective coordination through the carboxylate; the olefinic bond would be in a position accessible to intramolecular hydrogen transfer from the rhodium and, if coordination through the unsaturated bond occurs, the resulting chelate ring could enhance steric control. The carboxylates were also present as phosphobetaines (e.g., **10**, **11**) in systems containing excess phosphine (220).

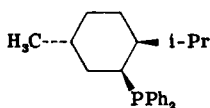


(10)

(11)

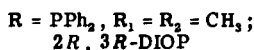
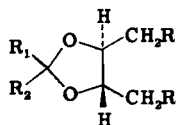


The nontrivial synthetic procedures to give the tertiary phosphines chiral at phosphorus (10) led Morrison's group (221, 222) to synthesize neomenthyldiphenylphosphine [(+)-NMDPP] (**12**) and led Kagan's group (10, 223, 224) to synthesize 2,3-*o*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane [(-)-DIOP] (**13**) from the commercially



NMDPP

(12)

2*R*, 3*R*-DIOP

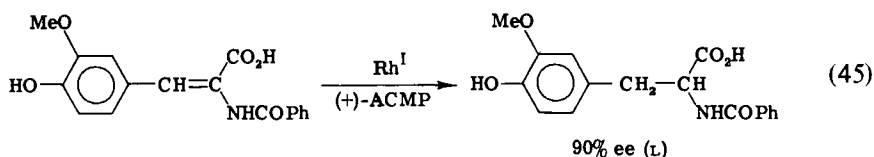
(13)

available, inexpensive, chiral precursors (-)-menthol and (+)-tartaric acid, respectively. *In situ* catalysts (P:Rh = 2) were usually formed from [Rh(monoolefin)₂Cl]₂ precursors in alcohol-benzene, and optimum optical purities of 60-80% were achieved for hydrogenation of some α,β -unsaturated acids, particularly for α -acyl (or aroyl)-aminoacrylic acids (223, 225):



² Optical purities and ee (enantiomeric excess) are used here synonymously, and express the excess of one enantiomer over the other; for example 50% ee means a 75%, 25% mixture of *R* and *S* forms.

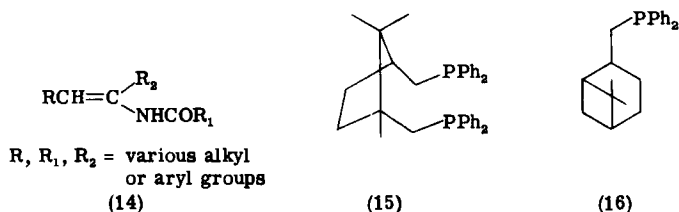
Hydrolysis of the —NHCOR^1 enamide group provides an excellent route to optically active amino acids including the important drug L-DOPA (3,4-dihydroxyphenylalanine). The (–)-DIOP catalyst system yielded the D-derivatives in excess, while the (+)-DIOP system gave the naturally occurring L-amino acids (225); the high stereoselectivities were attributed to conformational rigidity owing to the trans-fused dioxalane ring of the DIOP ligand and the metal-containing chelate ring. The Monsanto Company simultaneously developed efficient commercial syntheses for L-amino acids using rhodium(I) precursors with the chiral phosphine *o*-anisylcyclohexylmethylphosphine (ACMP) (226–228). The reactions using the (+)-*R*-ligand, run in methanol at 50°C and about 3 atm H_2 , yielded L-DOPA derivatives with optical purities up to 90%:



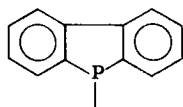
It is reported that 1 pound of catalyst yields 1 ton of L-DOPA, which is used to relieve the symptoms of Parkinson's disease in hundreds of thousands of sufferers of the shaking palsy. Other chiral phosphines of the ACMP type, but using other alkyl or aryl groups in place of the cyclohexyl and/or the methyl of the ether function, gave less effective asymmetric syntheses (11). The acylamino acids were considered to act as "tridentate" ligands, through the double bond and carboxylate to rhodium, and through amide hydrogen bonding to the phosphine ether group (11, 228). However, the DIOP system is almost as effective as the ACMP one under corresponding conditions (11), showing that extra bonding sites such as methoxy are not crucial. The substrates may be present as the free acid, or as carboxylate formed by the addition of triethylamine or sodium hydroxide. The carboxyl group is not essential for a high enantioselectivity because the enamides shown in 14 have been hydrogenated to up to 83% ee with the DIOP system in benzene-ethanol, and coordination through the enamide group was then suggested (225, 229). Changing from the mixed solvent to benzene alone for the *N*-acetyl- α -phenylethylamine enamide precursor, resulted in preferred formation of the opposite enantiomer (229).

Closely related to NMDPP are other chiral phosphines in which the diphenylphosphine moiety is attached to chiral carbon skeletons of naturally occurring compounds (10, 230–232). These include (–)-menthyl-diphenylphosphine (MDPP), (+)-1,2,2-trimethyl-1,3-bis(diphenylphosphinomethyl)cyclopentane (CAMPHOS, 15), and *cis*-myrtanyldiphenyl-

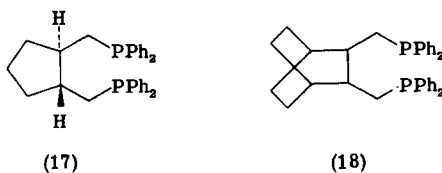
phosphine (MYRTPHOS, 16). The MDPP and CAMPHOS systems generally have lower activity and give lower asymmetric bias than the NMDPP catalyst (10, 232). Data on the use of 16 have not been published. Use of menthylmethylphenylphosphine (MMPP), chiral at both phosphorus and carbon, gives optical purities to 70% ee with α,β -unsaturated carboxylic acid substrates (232a). The stereoselectivities were stated to be greater than that using MDPP, and data using ligands *R* or *S* at phosphorus indicated that the configuration of the product was controlled by the stereochemistry at the phosphorus rather than the carbon.



Modification of DIOP by incorporation of a methyl group at the 3-position (meta) of each aromatic ring increased the optical yield to 90% from 80% for a DOPA precursor (224); inclusion of methyl at the 2-position or at the 2- and 5-positions, or using a phosphole derivative 13 with R =

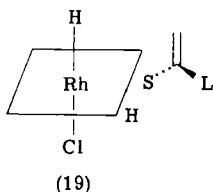


was less effective (224, 233). Variation of the remote R₁ and R₂ groups in compound 13 [e.g., R₁ = H, R₂ = Ph; R₁ = R₂ = (CH₂)₅] gave essentially the same data as for DIOP itself (224). Replacement of the acetone ring by carbon ring systems (17, 18) led to catalysts giving 63–80% ee with α -acylaminoacrylic acid substrates (224). The effect of changes in the ring size of the chelating diphosphines Ph₂P(CH₂)_nPPh₂ in 1:1 rhodium catalysts (i.e., P:Rh = 2) has been studied (233a) for comparison with the DIOP system (*n* = 4). For styrene in benzene, activity decreased in the order: PPh₃ > *n* = 3 > PPh₂Et > *n* = 1, 5 > *n* = 4, 6



$> \text{DIOP} > n = 2$ [replacement of $(\text{CH}_2)_n$ by *cis*- $\text{CH}=\text{CH}$ or CH_2OCH_2 gave poor catalysts]. For α -acetamidocinnamic acid in benzene/ethanol, the order was: $n = 4, 5 > \text{DIOP} > -\text{CH}_2\text{OCH}_2- > \text{PPh}_3, \text{PPh}_2\text{Et}, n = 3 \text{ or } 6 > n = 2 > -\text{CH}=\text{CH}-$, and the system with $n = 1$ was inactive.

From consideration of data for hydrogenation of *cis* and *trans* isomers of α, β -unsaturated carboxylic acids using ACMP, DIOP, NMDPP, MDPP, and CAMPHOS systems, Morrison *et al.* (10) concluded that matching of ligands with substrates for optimum ee is unpredictable; for example, there is not even a general stereocorrelation model apparent for the diastereomeric NMDPP and MDPP ligands, for these systems not only generate the "expected" enantiomeric products from the same substrate but sometimes generate products with the same chiralities (231).

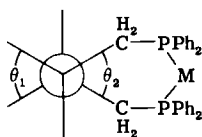


Glaser (234), however, has presented a stereocorrelation model for rhodium DIOP-catalyzed hydrogenations within a neutral octahedral complex, based on space-filling CPK-type molecular models, considering only steric effects [L = large substituent, S = small substituent in complex 19] and ignoring *cis-trans* geometry in the olefin. The model correctly predicted the stereochemistry of the major product of hydrogenation of all substrates $\text{RCH}=\text{C}(\text{S})\text{L}$ studied to 1975 except two [$\text{S} = \text{CO}_2\text{Me}$, $\text{L} = \text{Ph}$, $\text{R} = \text{H}$; and $\text{S} = \text{Et}$, $\text{L} = \text{Ph}$, $\text{R} = \text{H}$]. For a range of *Z*- α -acetamidocinnamate esters, the optical purity with $(-)$ -DIOP systems varied between 69 and 77% ee (*R*) with increasing size of the ester alcohol group through Me, Et, *i*-Pr, and *t*-Bu; the 1-adamantyl ester (a $\text{C}_{10}\text{H}_{15}$ moiety) gave only a 71% ee, but this was due to accompanying *Z,E* isomerization (235, 236). With the chiral alcohol moieties $(-)$ -menthyl and $(-)$ -bornyl, optical purities of 77 and 50% ee (*R*) were obtained (236, 237). Of interest is the finding that use of nonchiral phosphine catalyst systems, $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ [$n = 3-6$], with the chiral ester substrates gave optical purities up to 13.6% (237). Increasing bulk in the acyl function (NHCOR) of the *Z*-methyl- α -acylaminocinnamates gave decreasing optical purities in the *N*-acylphenylalanine methyl ester products; 69% ee ($\text{R} = \text{Me}$), 15% (*i*-Pr), 0% (*t*-Bu and 1-adamantyl). The smaller formamido group, however, gave only a 58% ee, while the trifluoroacetamido moiety larger than methyl now showed a reversal in chirality of the major product

isomer, and polar (electronic) interactions involving the amide carbonyl were thus invoked to account for these "anomalies" (238).

For *Z*- α -benzoylaminocinnamic acid and methyl ester substrates, with various donor and acceptor substituents in the phenyl ring, there was no correlation between the Hammett σ -values of para substituents and optical purity of the product (239). The DIOP systems hydrogenate *Z* isomers more rapidly than *E* isomers, and induce a greater optical bias. *N*-Acetyl substrates always gave higher optical purities than the *N*-benzoyl substrates, and similarly acid substrates were better than the corresponding methyl esters (239).

Some insight into the rhodium DIOP systems is gained from structural studies on the $\text{IrCl}(\text{1,5-COD})[(+)\text{-DIOP}]$ complex, which is a distorted trigonal bipyramid in which DIOP is an apical-equatorial bidentate ligand (the iridium atom is also asymmetric) (240). The configuration of the seven-membered iridium-containing chelate ring, in which the four phenyls appear in an alternating edge-face manner (see Fig. 2 below), was thought to result from the severe constraints of the acetone ring; the dihedral angles θ_1 and θ_2 in **20** (37° and 87° , respectively, in the iridium complex) were considered critical in determining the extent of asymmetric induction in DIOP-type systems. The structural data on the iridium complex were used to formulate schemes for asymmetric hydrogenation catalyzed by the neutral $\text{Rh}(\text{DIOP})\text{Cl}$ and cationic $[\text{Rh}(\text{COD})(\text{DIOP})]^+$ complexes, *assuming* that the catalyst precursor corresponds to a trigonal bipyramid structure like the iridium complex, but in which the cis-coordinated olefins of the COD ligand have been replaced by two hydrogen atoms. The key step was coordination of the substrate in a preferred conformation within neutral or solvated cationic octahedral complexes (240) (see below).

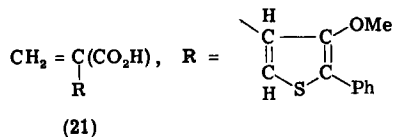


(20)

The cyclobutane and cyclohexane analogs of **17** have been made, and the (*1R,2R*)-carbocyclic diphosphine systems, with *Z*- α -acetamidocinnamic acid substrate, gave *N*-acetylphenylalanine with increasing ee [35 to 63 to 86% (*R*)] as the ring size decreased from 6 to 5 to 4 carbons (241), that is, with increasing torsional angle within the seven-membered rhodium-containing chelate ring (cf. structure **20**). The five-membered heterocyclic (*2R,3R*)-DIOP system gave 82% ee (*R*), intermediate be-

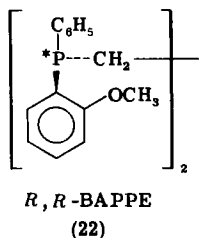
tween that for the C-4 and C-5 carbocyclic systems. With *Z*- α -acetamidocrylic acid substrate, the C-4, C-5 and DIOP systems were said (241) to give the same optical induction, 72–73% ee (*R*) (10, 225, 241), although one report (224) gives a value of 65% ee (*R*) for the C-5 system; nevertheless, the oxygen atoms and *gem*-dimethyl group in DIOP are clearly not crucial for high enantioselectivity (224, 241). Thus, it was concluded (241) that the phenyl ring in the acetamidocinnamic acid substrate in some way “senses” the differences in torsional angle of the more rigid diphosphines [a lower (40%) ee was obtained using the C-6 system with the substituted acrylic acid]. The torsional angle of 87° in the iridium-DIOP complex (20) lies between those of *trans*-1,2-cyclobutanedicarboxylic acid (99°) and *trans*-1,2-cyclopentanedicarboxylic acid mono-*N*-methyl amide (79°), which is at least consistent with the torsional model hypothesis, the dicarboxylic acid derivatives being taken as approximations to the C-5 and C-4 carbocyclic diphosphines (241).

The bulk of the ester group has little effect on optical purity of *N*-acetylphenylalanine ester products formed from the dehydro substrates using the C-4 catalyst, and with this or the DIOP system, variation of the substituent in the phenyl ring of the *N*-acetylphenylalanine precursors also had little effect (242).

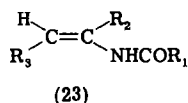


A thiophene derivative of acrylic acid (21) has been hydrogenated to 88% ee with a DIOP catalyst, the thiophene ring remaining unreduced (243).

The Monsanto group have used the cationic catalysts $\text{Rh}(\text{diene})(\text{diphosphine})^+$ (see Section II,B,1) with diphosphine (22), *R,R*-bis[(anisole)(phenylphosphine)] ethane (BAPPE), to reduce α -acylaminoacrylic acids in basic alcohol solution to products with 95–96% ee (244, 245).

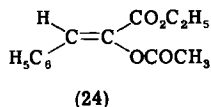


Unlike the corresponding ACMP and DIOP systems, for which optical purities generally increased with lower pressures and lower temperatures (11), the (22) systems were nonsensitive to these variables; this was attributed to formation of a rigid, five-membered ring between 22 and the rhodium (244). The *Z*-isomers of the α -acylaminoacrylic acids were all hydrogenated at much faster rates, and with greater enantiomeric excess than the *E*-isomers (all the products having the "natural" *S*-configuration). A range of other potentially tridentate substrates (23) and a thio-carbonylamino derivative [$-\text{NHC}(\text{S})\text{OC}_2\text{H}_5$] all gave good stereoselectivities; the prochiral substrates as usually prepared have the *Z*-geometry (245, 246). The bidentate substrates $\text{C}_6\text{H}_5\text{CH}=\text{CR}(\text{CH}_3)$, $\text{R} = \text{NHCOCH}_3$ or CO_2H , gave much lower enantiomeric excesses in products always



e.g., $\text{R}_1 = \text{C}_6\text{H}_5, \text{OC}_2\text{H}_5, \text{CH}_2\text{Cl}$
 $\text{R}_2 = \text{CN}, \text{CO}_2\text{C}_2\text{H}_5, \text{CO}_2\text{H}, \text{CONH}_2$
 $\text{R}_3 = \text{H}, n\text{-C}_3\text{H}_7, \text{C}_6\text{H}_5$

having the *R* configuration. Several comparisons showed again that the role of an amide is dominant to that of a carboxyl, but is not essential for high stereoselectivity, because the α -enol ester (24) gave 90% ee. The role of amide H-bonding to a phosphine methoxyl was deemphasized



because an *N*-methyl derivative of 23 ($\text{R}_1 = \text{C}_6\text{H}_5 = \text{R}_3$, $\text{R}_2 = \text{H}$) gave good stereoselectivity (60% ee), and direct attachment of amide to rhodium was preferred as the third binding site (245). A crystal structure of the $[\text{Rh}(\text{1,5-COD})(\text{diphosphine})]^+$ complex revealed an expected square planar structure ($\text{P}-\text{Rh}-\text{P} = 83^\circ$); the four phenyl groups, as in the iridium DIOP complex, again approximate an edge-face conformation around the metal with the rings containing the methoxyls exposing their face (Fig. 2), and it was suggested that the ether oxygens fix the conformation by interaction with the rhodium ($\text{O} \cdots \text{Rh} \sim 3.7 \text{ \AA}$) and possibly by interaction with hydrogens on the cyclic methylenes (245). The structure suggests that a linear and flat substrate would prefer to lie along the face-exposed *o*-methoxyphenyl groups. A conformation of the *Z*-enamide

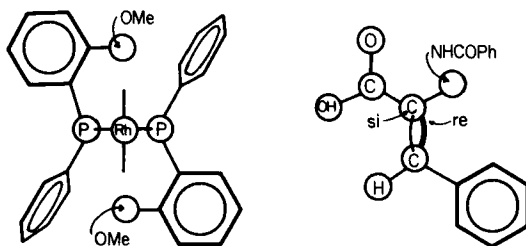
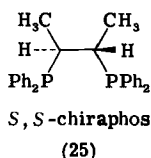


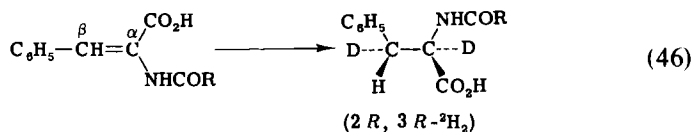
FIG. 2. Drawing showing the bisphosphine-rhodium complex viewed along the plane of the five-membered ring (diene omitted), and the *Z*- α -benzamido cinnamic acid substrate in a linear and flat conformation.

where the carboxyl, olefin, and the phenyl are coplanar (Fig. 2) will allow this if the amide oxygen binds to one of the equivalent rhodium axial positions and the olefin coordinates at an equatorial site. In this position the double bond exposes its *re*-face toward the metal and hydrogen transfer will give the *S*-isomer, the observed product. Exposure to the *si*-face results in the linear part lying along the edge-exposed phenyls where close approach and an efficient reaction is prevented. With the *E*-enamide, where the phenyl and hydrogen are interchanged, the phenyl will have to lie along an edge-exposed aryl group; close approach to the metal is prevented but a slow reaction still gives a predominance of *S*-isomer. The face-exposed phenyls, unlike the edge-exposed ones, also have π -electron density available for interaction with the substrate. Both steric and electronic factors are thus invoked (245).

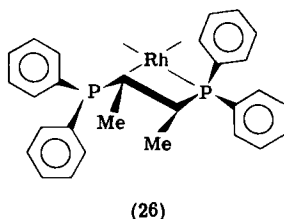


Remarkable success has been achieved by Fryzuk and Bosnich (247) using the complex $[\text{Rh}(\text{S},\text{S}\text{-chiraphos})(\text{COD})]^+$, where the chiral ligand 2*S*,3*S*-bis(diphenylphosphino)butane, a diphosphine chiral at carbons (25), is readily synthesized from 2*R*,3*R*-butane diol. The *Z*-isomers of the prochiral α -*N*-acylaminoacrylic acid substrates were hydrogenated at ambient conditions to *R*-products with very high enantiomeric excess; indeed, leucine and phenylalanine derivatives were obtained in *complete optical purity*. Catalytic deuteration was shown to lead to pure chiral β -carbon centers as well as α -carbon centers in the leucine and phenylal-

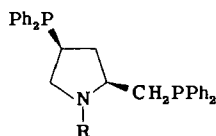
anine systems, e.g.:



A crystal structure of the cation (248) shows the preferred *S,S*-conformation (26), the methyl groups being equatorially disposed to give the



static five-membered δ -chelate ring. It was suggested (247) that the orientation of the phenyl groups held by the puckered chelate ring was responsible for the diastereotopic interaction that discriminates the prochiral faces of the substrate. The data require that the *S,S*-chiraphos system prefers coordination of the α -*si*, β -*re* face of the substrate, but this was not obvious from models. The explanation, however, must be very similar to that presented by the Monsanto group (245) (cf. Fig. 2). The Bosnich catalyst yields the "unnatural" amino acids, but use of *R*-1,2-bis(diphenylphosphino)propane, abbreviated *R*-prophos, was said to give the "natural" amino acids in similar high optical yields (247).

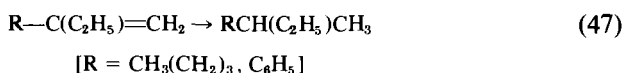


PPM: R = H
 BPPM: R = CO₂-*t*-Bu
 CPPM: R = CO₂C₂₇H₄₅

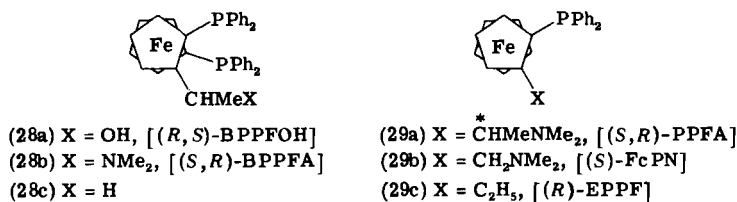
(27)

Other phosphine systems have been reported in which four phenyl groups are oriented around a rhodium center (249-254). They all hydrogenate *Z*-enamides efficiently, and intermediates with a conformation of edge-face phenyls seem plausible in each case. The *2S,4S*-4-diphenyl-

phosphine-2-diphenylphosphinomethylpyrrolidine (PPM) and related *N*-butoxycarbonyl derivative (BPPM) systems of Achiwa (249–251) are chiral at carbon atoms (27), and are formed from naturally occurring L-hydroxyproline. The *in situ* 1:1 Rh/BPPM catalyst with added triethylamine gave optical yields up to 91% for reduction of substituted cinnamic acids to various alanines (usually the D-form) at 50 atm hydrogen pressure in ethanol (249). The *N*-cholesteryloxycarbonyl derivative (CPPM) renders the rhodium complex soluble in aliphatic hydrocarbons; this “lipophilized” system was used to hydrogenate terminal olefins (as neat substrates) to up to a 24.7% ee (250):



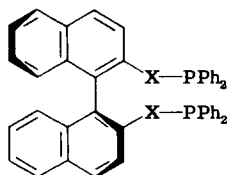
Kumada's group (252, 255, 256) has synthesized a range of ferrocenyl-phosphine ligands (28, 29) initially for use in asymmetric hydrosilylation.



Ligands such as 28c, 29b, and 29c are not chiral at phosphorus or carbon but possess a planar element of chirality. The corresponding dimethylphosphine derivative of 29a [(*R,S*)-MPFA] was also made (255); the first-mentioned chirality refers to the carbon substituent, and the second to that of the disubstituted ferrocene moiety. The hydrogenation conditions used were similar to those used by Achiwa (249), but no triethylamine was added; up to 94% ee was achieved for L-alanine derivatives using the [(*S,R*)-BPPFA] system in aqueous alcohol media. Enhanced optical induction in the aqueous media was attributed to interaction of the amino group of the coordinated phosphine with the olefinic carboxy group (252). Optical purity data from nickel(II)-catalyzed cross-coupling of Grignard reagents with alkenyl halides using ligands 29a and 29b imply that, at least for this process, the dominant chiral element is that of the ferrocene rather than that of the carbon (256). The cationic complexes [(diene)Rh(PPFA)]⁺, with both (*S,R*)- and (*R,S*)-PPFA, have been used at ambient conditions in alcohol solvents to hydrogenate α -acetamidocinnamic and α -acetamidoacrylic acids to products with 84% and 58% ee, respectively (257); the crystal structure of the (*S,R*)-PPFA ligand (258) shows that the methyl group on the asymmetric carbon is directed away from the cyclopentadiene (Cp) rings, and of interest the two Cp rings are

eclipsed whereas in ferrocene itself they are staggered. An octahedral intermediate $[\text{H}_2\text{Rh}(\text{PPFA})(\text{substrate})]^+$, in which the substrate was coordinated via both olefinic and amide carbonyl links, and the ligand by phosphorus and nitrogen, could account for the configuration of the products (257).

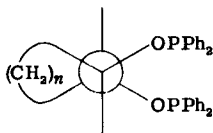
A new class of phosphines (**30**) containing only an axial element of chirality (atropisomerism) has been made (253, 254). An *in situ* 1:1 rhodium/2,2-bis(diphenylphosphinomethyl)-1,1'-binaphthyl system (**30a**) hydrogenated α -acetamidocinnamic acid to a 54% ee (*S*) using 50 atm H_2 , the solvent not being recorded (253). The corresponding diphenylphosphinite system (**30b**) in toluene-acetone was particularly effective (76% ee) for hydrogenation (95 atm) of α -acetamidocinnamic and α -acetamidoacrylic esters (254).



(**30a**) $\text{X} = \text{CH}_2$ [(*S*)-NAPHOS (1, 1)]

(**30b**) $\text{X} = \text{O}$

C-Chiral diposphinites based on cyclohexane and cyclopentane rings (**31**) (cf. structure 17) have been used in 1:1 rhodium complexes at 50 atm H_2 in unspecified solvents (259, 260).



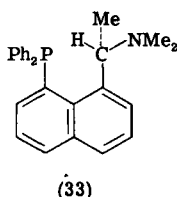
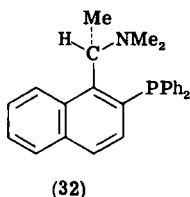
(**31a**) $n = 4$, *trans*-1,2-bis(diphenylphosphinoxy)cyclohexane [BDPCH]

(**31b**) $n = 3$, *trans*-1,2-bis(diphenylphosphinoxy)cyclopentane [BDPCP]

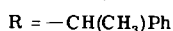
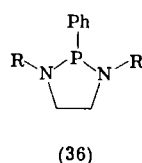
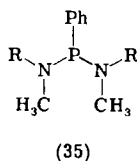
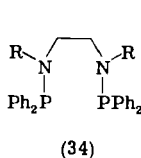
The BDPCH system was again effective for the α -acetamido olefinic acids (up to 79% ee, which could be increased to nearly 100% ee after recrystallization of the *N*-acetylamino acid products), while the BDPCP system gave 60% ee for hydrogenation of α -ethylstyrene which is one of the highest ee values yet recorded for a substrate containing no polar substituents ($-\text{COOH}$, CONHR) (see also Section IV,B).

The use of aminophosphines with rhodium(I) for catalytic hydrogenation was established some years ago, especially by Stern *et al.* (261; also

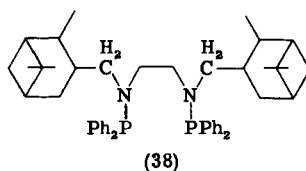
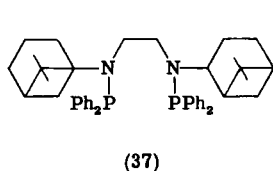
1, p. 234). As well as catalysts based on the ligands illustrated in **27**, **28b**, **29a**, and **29b**, systems based on **32** and **33** have given optical purities up



to 40% with amino acid precursors (262). The ligands **34–36** have been obtained from optically active α -phenylethylamine derivatives (263, 264). Use of **34** led to optical yields similar to those obtained using DIOP, at

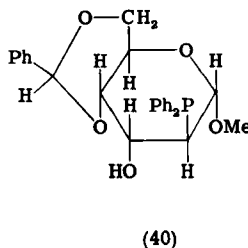
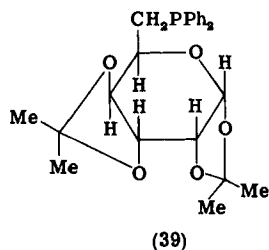


least for amino acid precursors (263, 264); the other aminophosphine systems gave <20% ee (264). The bidentate aminophosphines (**37** and **38**) derived from the terpenes (–)-nopinylamine and (–)-pinane-3-carboxylic acid, respectively, have been made for intended use in asymmetric hydrogenation (232).

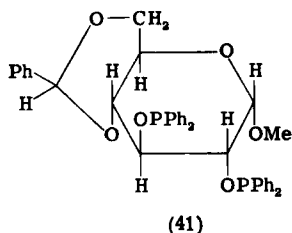


In situ rhodium(I) complexes containing both triphenylphosphine and optically active amines are said to effect asymmetric hydrogenation of the amino acid precursors (265).

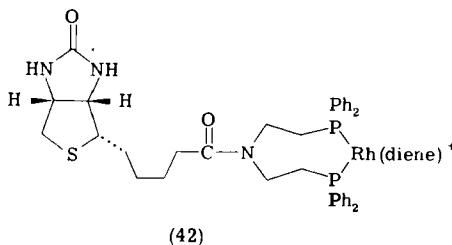
Sugars offer themselves as readily available chiral ligands, and rhodium(I) catalysts, with the phosphine ligands **39** and **40** derived from D-galactose and D-altrose, respectively, give up to 40% ee for hydrogenation of α,β -unsaturated carboxylic acids (266). A cationic complex containing the diphosphite **41** based on D-glucose is effective at ambient conditions for acetamidoacrylic acid and ester substrates (up to 80% ee),



while substrates without the acetamido substituent were not hydrogenated at all (267).



A very interesting development is the incorporation of an achiral diphosphinerhodium(I) moiety at a specific site in the protein avidin (268). The protein binds biotin, which was first converted to the cationic rhodium complex shown in **42**. α -Acetamidoacrylic acid was converted to *N*-acetylalanine with 40% ee in aqueous solution at pH 7 (0°C, 1.5 atm H_2).



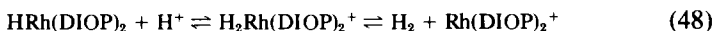
2. The Nature of the Catalysts

The nature of the catalysts, especially those formed *in situ* from chlororhodium(I) precursors, deserves some comment. The catalysts have been often written as $Rh(P^*)_2Cl(\text{solvent})$, where P^* and $(P^*)_2$ represent monodentate and bidentate chiral phosphines, respectively (10), but this almost certainly pertains for nonpolar media only. In polar media, including the mixed hydrocarbon/alcohol solvents usually employed,

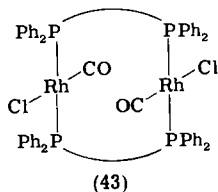
$\text{Rh}(\text{diene})(\text{P}^*)_2^+$ cation precursors are formed (133, 134; also 1, p. 270), and indeed such complexes may be used in place of the *in situ* catalysts in either media (11, 244, 269-271).

Under H_2 , conversion to $\text{H}_2\text{Rh}(\text{P}^*)_2(\text{solvent})_2^+$ has usually been *assumed*, as demonstrated for corresponding complexes such as $\text{Rh}(\text{PPh}_3)_2(\text{diene})^+$ (Section II,B,1). However, it has recently been noted (272) that a $\text{Rh}(\text{diene})(\text{DIOP})^+$ system in acetone reacts with H_2 to yield only $\text{Rh}(\text{DIOP})(\text{acetone})_2^+$; that is, there is no subsequent dihydride formation. The analogous $\text{Rh}(\text{diene})(\text{diphos})^+$ cation behaves similarly (see Section II,B,1). Differences in behavior of the bismonophosphine and monodiphosphine catalysts will likely lead to differences in hydrogenation mechanisms, for example, in terms of unsaturate or hydride routes, although both lead to $\text{H}_2\text{Rh}(\text{olefin})(\text{phosphine})_n$ intermediates [Eq. (1)]. Paths through monohydride catalysts [see Eq. (25)] cannot be excluded, however (133, 273), especially because bases are frequently used as cocatalysts. Base may also convert carboxylic acids to the salts, and carboxylate complexes such as $\text{Rh}(\text{DIOP})(\text{OCOR})$ could be present (239).

The bis-DIOP complex $\text{HRh}[(+)\text{-DIOP}]_2$ has been used under mild conditions for catalytic asymmetric hydrogenation of several prochiral olefinic carboxylic acids (273-275). Optical yields for reduction of *N*-acetamidoacrylic acid (56% ee) and atropic acid (37% ee) are much lower than those obtained using the mono-DIOP catalysts (10, 11, 225). The rates in the bis-DIOP systems, however, are much slower, and the hydrogenations are complicated by slow formation of the cationic complex $\text{Rh}(\text{DIOP})_2^+$ (271, 273, 274) through reaction of the starting hydride with protons from the substrate; under H_2 the cationic dihydride is maintained [cf. Eq. (25)]:



Itaconic acid was hydrogenated rapidly to a 20% ee, and kinetic and spectrophotometric studies on this system were interpreted in terms of a mechanism involving a standard unsaturate route [cf. Eq. (5)]. The actual catalyst was thought to be $\text{HRh}(\text{DIOP})(\text{DIOP}^*)$, where DIOP^* represents a monodentate DIOP with one dangling $-\text{CH}_2\text{PPh}_2$ moiety (273, 275). Rhodium(I) carbonyls (276) and ruthenium(II) complexes (90, 275) (Section III,B) containing monodentate DIOP have been isolated.



The occurrence of multinuclear catalysts in hydrogenations catalyzed by rhodium-DIOP systems seems unlikely, although the *trans*-RhCl(CO)(DIOP) complex **43** is dimeric (276), and in basic methanolic solution the 1:1 diphos complex exists as $\text{Rh}_3(\text{diphos})_3(\text{OMe})_2^+$ (138a, Section II,B,1).

3. Ketone and Imine Substrates

Since the Osborn-type cationic dihydride catalysts $\text{H}_2\text{RhL}_n\text{S}_y^+$ [see Eq. (24)], containing more basic phosphines such as PPh_2Me , PPhMe_2 , and PMe_3 , were found effective for hydrogenation of saturated ketones in the presence of small amounts of water (130; also 1, p. 270), several groups have incorporated chiral phosphines into such species, usually via $\text{Rh}(\text{diene})\text{L}_2^+$ complexes, for attempted production of optically active alcohols. Use of PPhMeR (R = benzyl or ethyl) or DIOP gave <9% ee with acetophenone, 2-ketones, and pyruvic acid [Eq. (49)] as substrates (269, 277–279), while the ACMP ligand gave optical purities up to 56% ee, this being dependent on solvent and water content (280). The latter system has also been used to reduce a cyclopentane-trione to an *R*-hydroxycyclopentane-dione, a precursor for prostaglandin E (281). *In situ* catalysts formed from neutral rhodium(I) precursors, or $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in the presence of base, with the same phosphines (R = benzyl or propyl) have given much higher optical yields with acetophenone (up to 29% ee), while a similarly formed DIOP catalyst gave a 51% ee (282); tris(2-methylbutyl)phosphine with C-chirality was ineffective.

Use of the BPPFOH ligand (**28a**) in a cationic rhodium(I) catalyst has given optical yields as high as 83% ee for hydrogenation (50 atm) of pyruvic to lactic acid (279); related ligands without the polar hydroxy group (e.g., **28b** and **28c**) gave only 16% ee, indicating participation of the hydroxy group. Pyruvates are also converted to lactates in about 65–75% ee using the BPPM and CPPM ligands (**27**) (99, 250, 283), and in about 42% ee using a neutral DIOP catalyst (99). Hydrolysis of the products obtained from asymmetric hydrogenation of α -enol esters also provides an efficient route to chiral alcohols, and, for example, (*S*)-3-phenyllactic acid is obtained in 90% ee from the hydrogenation of **24** using the BAPPE ligand (**22**) (245). Systems using the BDPCP ligand (**31**) give an optical yield of 22% ee with acetophenone (260).



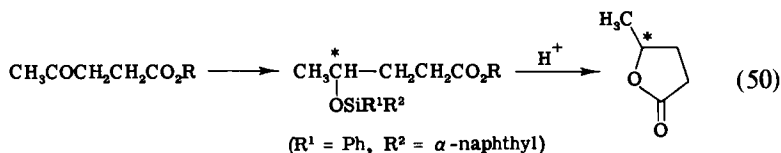
The imine group in the Schiff base $\text{PhMeC}=\text{NCH}_2\text{Ph}$ has been hydrogenated to the amine with 22% ee using the cationic DIOP complex in

alcohol solvents (269), while a benzyl(methyl)phenylphosphine system gave only very low optical yields with such substrates (100).

4. Ketone and Imine Reductions via Hydrosilylation

As outlined in Section II,E, ketone and imine groups are readily hydrogenated via a hydrosilylation-hydrolysis procedure. Use of chiral catalysts with prochiral substrates, for example, $R_1R_2C=O$ or $R_1R_2C=N-$ leads to asymmetric hydrosilylation (284, 285; Chapter 9 in this volume) and hence optically active alcohols [cf. Eq. (41)].

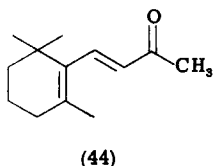
Cationic systems with benzyl(methyl)phenylphosphine (285-293) and DIOP (289-291, 294-296) have been extensively studied. Optical enrichment up to 60% ee has been attained with alkyl phenyl and mixed alkyl ketones, while pyruvate and glyoxalate substrates $R^1COCO_2R^2$ ($R^1 = CH_3, Ph$; $R^2 =$ alkyl or menthyl) gave products with optimum optical yields in the range 60-85% ee. The chiral menthyl group gave no great advantage over a propyl group (285, 289, 290). Use of the achiral ligand system $RhCl(PPh_3)_3$ gave up to 20% ee for reduction of (-)-menthyl phenylglyoxylate (285). The higher optical yields attained with α -keto esters compared to the simple prochiral ketones may be due to coordination of the ester group (285). Acetoacetates (CH_3COCH_2COOR) and levulinates ($CH_3COCH_2CH_2COOR$) could then give rise to five- and six-membered ring chelate intermediates, respectively; the former substrates, however, gave optical yields similar to those obtained with simple ketones, while the levulinates gave γ -butyrolactones of high optical activity (84% ee):



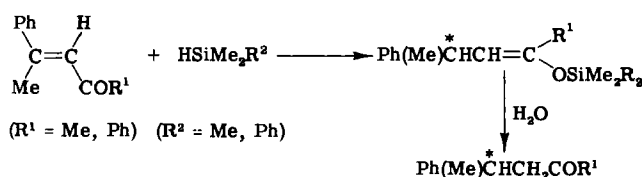
The low induction for the acetoacetates was attributed to a transfer hydrogenation process within an enol form of the substrate, coordinated through the carbon-carbon double bond, $CH_3C(OH)=CH-CO_2R$, rather than hydrosilylation of the carbonyl moiety (285).

Use of the same benzyl(methyl)phenylphosphine and DIOP rhodium(I) catalysts with α,β -unsaturated carbonyls has led to some interesting selectivity patterns (297, 298). Dihydrosilanes undergo 1,2-addition at the carbonyl of substrates such as 2-methylcyclohexenone, mesityl oxide,

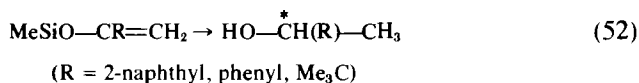
and β -ionone (**44**), and the hydrogenation products are the α,β -unsaturated alcohols with up to 43% ee (**286**). Monohydrosilanes, however, undergo 1,4-addition to products which hydrolyze to optically active saturated ketones with up to 16% ee (**293**):



(51)

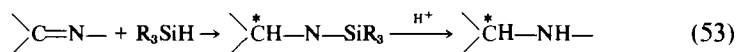


Hydrogenation of silyl enol ethers with the DIOP catalyst followed by hydrolysis [Eq. (52)] has yielded a route to optically active alcohols with low optical purities, ~7% ee; NMDPP (**12**) and MePhPR (R = *n*-Pr, Et, benzyl) systems were less effective (**299**).

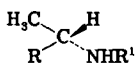


Menthone and camphor undergo asymmetric hydrosilylation to give alkoxysilanes with up to 82% optical purity using neutral rhodium(I) catalysts containing DIOP or neomenthyl- or menthyl-diphenylphosphine; even triphenylphosphine gave about 65% ee (**300**). Hydrolysis to alcohols was not reported. The ferrocenyl ligands (**28**, **29**) are similarly effective for asymmetric hydrosilylation (**255**), and could be used for production of the optically active alcohols.

The most efficient way to produce optically active amines, at least with a rhodium-DIOP catalyst, is via the hydrosilylation-hydrolysis process (**229**, **284**, Chapter 9 in this volume); for example:

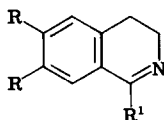


Secondary amines such as **45** have been made with up to 65% ee, while aromatic imines of the type shown in **46** give products with up to 39% ee (**229**).



R, R¹ = aryl

(45)

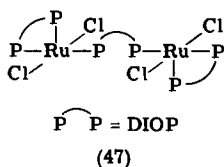


R = H, OMe;
R¹ = CH₃, benzyls

(46)

B. Other Transition Metal Catalysts with Chiral Phosphines

In spite of the high catalytic activity of the $\text{RuCl}_2(\text{PPh}_3)_3$ - $\text{HRuCl}(\text{PPh}_3)_3$ system (Section II,A), other $\text{RuCl}_2(\text{PRPh}_2)_n$ complexes [$n = 3$ or 4 ; R = Me or $\text{MeCH}_2\text{CH}^*(\text{Ph})\text{CH}_2$] are not efficient for hydrogenation even in the presence of a base to promote hydride formation (301) [cf. Eq. (4)]. An exchange reaction using $\text{RuCl}_2(\text{PPh}_3)_3$ and DIOP, however, leads to the bridged complex **47** that has five-coordinate square pyramidal geometry at each ruthenium:



This complex effects asymmetric hydrogenation of α,β -unsaturated carboxylic acids with up to 60% ee, the active catalyst being $\text{cis-HRuCl}(\text{DIOP})_2$ (275, 301, 302). The bis(diphenylphosphino)butane ligand $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 4$), comparable to DIOP, again gives a bridged complex like **47** (303), while ligands with $n = 1-3$ give octahedral $\text{trans-RuCl}_2(\text{diphosphine})_2$ complexes and the corresponding catalytically inactive hydrides which are now $\text{trans-HRuCl}(\text{diphosphine})_2$ species (275, 302). Two DIOP ligands, each with four carbon atoms between the phosphorus donors, do not go trans, at least in octahedral ruthenium(II) systems, presumably because of steric problems. The $\text{cis-HRuCl}(\text{DIOP})_2$ complex operates by the familiar mechanism of Eq. (5), the phosphorus trans to hydride likely being labilized (275). A complex $\text{RuCl}_2(\text{DIOP})_2$ has been synthesized, but one of the DIOP ligands is monodentate and five-coordinate geometry again persists; the complex readily forms the $\text{cis-HRuCl}(\text{DIOP})_2$ catalyst (275).

The cluster complex $\text{H}_4\text{Ru}_4(\text{CO})_8(\text{DIOP})_2$ has been used at $\sim 150^\circ\text{C}$ with 100 atm H_2 for asymmetric hydrogenation of acetophenone and methyl-

ethylketone to alcohols, and of the oxime derivatives to the amines [Eq. (54)] (304); optical yields were low and reached a maximum of 14.5% for the oxime with $R = t\text{-Bu}$. The complex also effects hydrogenation of prochiral α,β -unsaturated acids to products with optical yields upto 60% ee; the reactions also yield small amounts of γ -lactones [cf. Eq. (18)] (305, 306).



Compared with the Osborn-type cationic rhodium complexes (Section III,A,3), the iridium analogs are much less active for asymmetric hydrogenation of ketones (280).

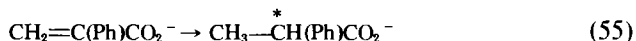
Platinum(II) complexes such as $[\text{PtCl}_2(\text{PhMePR})_2]$ ($R = \text{benzyl or propyl}$) have been used for asymmetric reduction of phenylketones to alcohols with up to 19% ee via the consecutive hydrosilylation–hydrolysis process (Section III,A,4) (211, 307). A nickel(II) complex with the benzylphosphine, and palladium(II) phosphine complexes did not catalyze the hydrosilylation (211).

C. Catalysts with Chiral Ligands Other than Phosphines

Besides the major thrust using chiral phosphine catalysts, other chiral ligands have been used with rhodium and other metals for asymmetric hydrogenation.

The use of chiral amide ligands has been restricted to rhodium, where the catalyst precursor is $[\text{Rh}(\text{BH}_4)(\text{amide})\text{py}_2\text{Cl}_2]$. The work has been reviewed (10, 35); cinnamate derivatives were reduced to up to 57% ee, and hydrogenation of a carbon–nitrogen double bond in folic acid leads to tetrahydrofolic acid with high biological activity (308).

Cyanoaminocobaltate(II) catalysts (I, p. 150) were initially studied in relation to the well-known activity of $\text{Co}(\text{CN})_5^{3-}$ (I, p. 106). Use of such catalysts with optically active amines (1,2-propanediamine and *N,N*-dimethyl-1,2-propanediamine), thought to be bridged in complexes such as $[(\text{CN}_4)\text{Co-amine-Co}(\text{CN}_4)]^{4-}$, led to asymmetric hydrogenation of atropate [Eq. (55)] to a 7% ee (309).

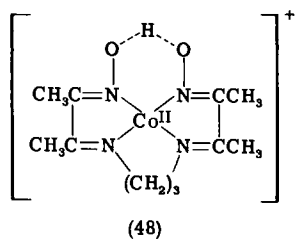


Use of optically active amino acids with $\text{Co}(\text{CN})_5^{3-}$ gave negligible optical induction (310).

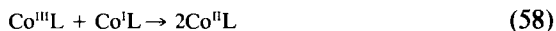
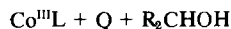
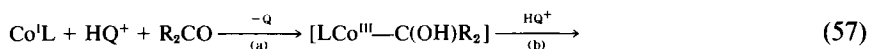
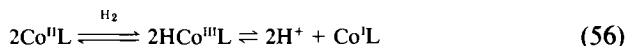
The use of optically active amines in bis(dimethylglyoximate)cobaltate(II)amine systems (Section II,C) has led to asymmetric reduction

of the olefinic bond in α,β -unsaturated ketones and esters (up to 50% ee), and to asymmetric reduction of carbonyl in α -diketones and α -oxo esters (up to 80% ee) (311-314). Hydroxyamine alkaloids such as quinine, cinchonidine, and ephedrine were the most effective bases, while amines not containing hydroxyl (*o*-acetylquinine, brucine, 1,1-phenylaminoethane) gave small or zero optical yields, and secondary bonding via the hydroxyl of a noncoordinated alkaloid and carbonyl of the substrates is likely (see Fig. 3 below). Use of quinoline and quinine, which differ in chirality at the α -hydroxy group, gave *R*- and *S*-forms of benzoin, respectively, from hydrogenation of benzil. Oxo esters yielded chiral reductive dimerization products as well as the expected hydroxy esters.

Closely related to the dimethylglyoximate (DMG) systems is that using the Schiff base ligand derived from 2,3-butanedione monooxime and 1,3-propanediamine (48) (315).



In the presence of benzylamine, which coordinates trans to an active site, and quinine, the noncoordinated chiral component, optical purities up to 80% ee were again attained for hydrogenation of benzil. Convincing evidence was presented for the mechanism outlined in Eqs. (56)-(58), where L is the macrocyclic ligand, Q is quinine, and R = Ph (benzylamine, and charges of the complexes are omitted):



The stereochemistry of the product is determined by step a, in which the proton is transferred from the quinine to the coordinated carbonyl, and the quinine is considered associated with the substrate making it more susceptible to nucleophilic attack by the cobalt(I) (Fig. 3). The mechanism is analogous to some biological oxidoreductase systems, where the site that determines the stereochemistry is remote from the active cata-

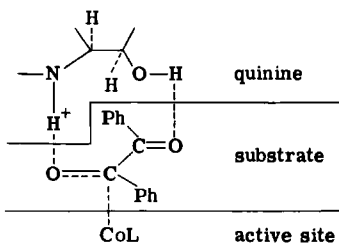
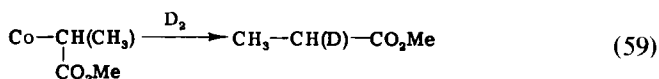


FIG. 3

lytic site (313, 315) [see also the rhodium-protein system (42) described in Section III,A,1].

Mechanisms involving axial coordination of the optically active amine have also been invoked, and crystal structure data on $\text{RCo}(\text{DMG})_2\text{B}^*$ complexes, where R is alkyl or (*R*)-1-(methoxycarbonyl)ethyl, and B^* is (*R*)- α -methylbenzylamine, were obtained (316, 317). Because deuteration of the (*R*)-methoxycarbonyl complex gave (*S*)-methylpropionate-2-d, it was concluded that $\text{Co}-\text{C}$ bond cleavage occurred with inversion of configuration at the carbon (317). It would be useful to know the mechanistic details of this step, which could involve attack by D^+ , $\text{DCo}(\text{III})$, or coordinated D , as well as D_2 , for it is an unusual, if not unique, observation [contrast with the usual retention mechanism outlined in Eq. (39)].

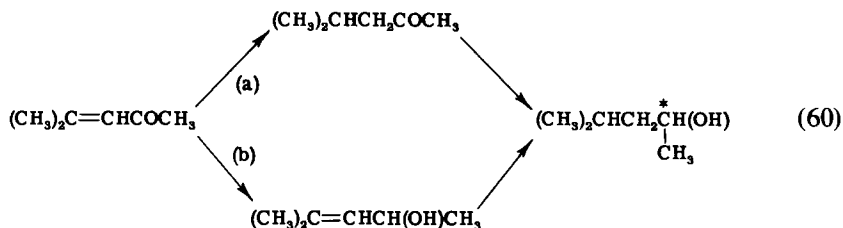


Cationic rhodium(I) and iridium(I) of the type $\text{M}(\text{N}-\text{N}')(\text{diene})^+$, where $\text{N}-\text{N}'$ represents Schiff bases of pyridine-2-aldehyde, have been synthesized, including some derived from optically active amines (318). Because the corresponding bipyridine and phenanthroline analogs, e.g., $\text{Rh}(\text{phen})(\text{diene})^+$, are active hydrogenation catalysts (see Section XI), the Schiff base systems seem promising for asymmetric catalysis, although a cobalt carbonyl catalyst containing chiral *N*- α -methylbenzyl-salicylaldehyde induced zero asymmetry in a hydrogenation of α -ethylstyrene (63).

The chiral amine complex $\text{cis-PtCl}_2(\text{C}_2\text{H}_4)[(\text{S})-\text{PhMeCHNH}_2^*]$ has been used for hydrogenation of phenylketones to the alcohols via the hydrosilylation-hydrolysis procedure (Section III,A,4), but optical yields were very low (211).

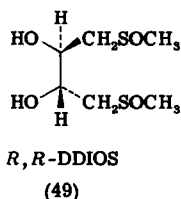
Use of ruthenium(III) chloride with poly-L-methylethylenimine is said to give a homogeneous catalyst for asymmetric reduction of the keto

group in methylacetoacetate (up to 5.3% ee), and of mesityl oxide (10, 319):



The major path via **a** gives inactive alcohol product, but a slight contribution via **b** was thought to give rise to the observed low optical purity, possibly as a result of bidentate coordination. [This system is possibly a "supported" catalyst (see Section IV, B)].

Monodentate sulfoxide ligands $\text{R}^1\text{R}^2\text{SO}$ with chirality at either the sulfur ($\text{R}^1 = \text{Me}$ or *t*-Bu, $\text{R}^2 = p$ -tolyl) or in an alkyl side chain, have been coordinated to ruthenium(II) (275, 320) and rhodium(I) centers (140a, 275) in attempts to synthesize effective asymmetric hydrogenation catalysts. A maximum optical yield of 15% ee was reported for α,β -unsaturated acid substrates using a trimeric $[\text{RuCl}_2(\text{MBMSO})_2]_3$ complex, where MBMSO is *S*-bonded 2-methylbutyl methyl sulfoxide, chiral at C-2 and racemic at the sulfur. Kinetic data showed the catalyst to be a monomeric species. Somewhat better yields (up to 25% ee) have been obtained using ruthenium(II) complexes containing chelating chiral sulfoxides analogous to DIOP, e.g., structure **13** with $\text{R} = \text{SOCH}_3$, which was called DIOS (275, 321). The most effective complex was $\text{RuCl}_2(\text{DIOS})(\text{DDIOS})$, where DDIOS is the acetal-cleaved derivative (**49**); the complex is thought to have a bidentate *S*-bonded DDIOS and a bidentate DIOS coordinated through one sulfur and one oxygen (321).



A rhodium complex $(\text{NBD})\text{Rh}(\text{PPh}_3)(\text{DIOS})^+$ was active via $\text{H}_2\text{Rh}(\text{PPh}_3)(\text{DIOS})^+$, but there was no optical induction with unsaturated acid substrates, which possibly displace the chiral ligand (275). The DIOS-type ligands have not yet been resolved at the sulfur. The extent

that a platinum(II) S -bonded p -tolyl methyl sulfoxide (chiral at sulfur) distinguishes between the prochiral faces of a coordinated olefin in *cis*-Pt(sulfoxide)(olefin)Cl₂ complexes has been studied and is generally small, although quite large discrimination is observed for olefinic rotation barriers (322).

Catalysts such as HRuX(PPh₃)₃, where X is an optically active carboxylate (e.g., *R*-mandelate) gave only 0.4% ee using 2-ethylhex-1-ene as substrate (124). Soluble Ziegler-Natta catalysts comprised of triisobutylaluminum with the optically active alkoxide complex, titanium tetra-(–)-menthoxide, hydrogenated racemic terminal olefins such as 3,4-dimethylpent-1-ene, but with zero ee (323).

Chiral hydroxamic acids (324) seem potentially useful ligands but they have not been used in hydrogenation catalysts.

IV

SUPPORTED TRANSITION METAL COMPLEXES AS CATALYSTS

This subject has been well reviewed recently, including an article (27) within this series (6, 14-29), and so this section will briefly summarize the general conclusions from these reviews and more recent literature concerning hydrogenation catalysts. The description as "heterogenized-homogeneous catalysts" (15, 16), although somewhat of a tongue twister, is a good one in that the typical homogeneous catalyst (a discrete molecular compound usually operating under mild conditions) is chemically bonded through one or more ligand sites to an insoluble polymer support, in this sense becoming heterogeneous. Their use can in principle couple the advantages of homogeneous catalysts (efficiency, in that all metal atoms are available as catalyst; reproducibility; and specificity and controllability by ligand variation) to those of heterogeneous catalysts (good thermal stability, no solvent restrictions, and, most important of all, ease of separation from the reaction products) (27). Poisoning by products has been considered a potential disadvantage of homogeneous catalysts (27), and indeed even "poisoning" of the catalyst by side reactions with substrate can occur, e.g., carbonylation of the RhCl(PPh₃)₃ catalyst to inactive RhCOCl(PPh₃)₂ during hydrogenation of α,β -unsaturated aldehydes (116, 325, 326). Nevertheless, a serious problem with heterogeneous catalysts, poisoning by sulfur, may not be so serious in homogeneous systems (1, p. 228; 327, 328).

A. *Nonasymmetric Hydrogenations*

The review of Hartley and Vezey (27) summarizes the various support materials that have been used together with metal complexes, usually Group VIII systems, for catalysis generally. The most commonly used support has been polystyrene cross-linked with divinylbenzene containing substituents such as phosphino or amino for covalent binding to the metal. Cyanomethyl, thiol, and cyclopentadienyl substituents have also been used as functional groups, and systems in which the metal is linked directly via π - or σ -bonding to the phenyl groups of various polystyrenes have been studied. In addition to polystyrene, other organic supports have been used. Of these, some already contain donor ligands (oxygen or nitrogen), e.g., polymers of acrylic acid, vinyl alcohol, vinylpyridines, vinylamine, methylethylenimine, and various Schiff bases; other supports, including polyvinyl chloride, polybutadiene, polyvinyl alcohol, and cellulose, have been modified by introduction of ligand donors, usually a phosphine.

Other covalently bonded catalysts are those on inorganic supports such as silica, molecular sieves (zeolites), and alumina, the complexes being held either directly via the oxygen of surface hydroxy groups or via an intermediate functional group, again especially phosphino.

Ionically bound complexes on sulfonated or aminated ion-exchange resins have been used, as have complexes adsorbed (van der Waals forces) onto silica gel and other supports.

Table II in Reference (27) summarizes hydrogenations catalyzed by supported metal complexes that were reported up to early 1975. Rhodium complexes on phosphinated supports feature prominently, the rhodium being introduced as RhCl_3 , $\text{RhCl}(\text{PPh}_3)_3$ and analogs, $\text{HRh}(\text{CO})(\text{PPh}_3)_3$, or rhodium(I) diene or olefin precursors. Because H_2 readily reduces rhodium to the univalent state (1, pp. 201 and 275), the supported catalysts are akin to the $\text{RhCl}(\text{PPh}_3)_3$ type (Section II,A) or the $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ type (1, p. 250). Also listed were three reports on iridium(I) analogs, and six reports on supported palladium(II) or platinum(II) chlorides, some involving phosphine donors. Nickel(II) had been incorporated into phosphinated polyvinyl chloride, and ruthenium(II) as $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$ into phosphinated polystyrene. Rhodium(III) had also been used in polyacrylic acids and esters, and finally, incorporation of a cyclopentadienyl moiety into a polystyrene had led to a supported titanocene catalyst (27).

From the data available, Hartley and Vezey (27) discussed the variable parameters. The type of support material is important. On phosphinated silica, the complex is on the outside the surface and is more accessible

and less selective to reactants than when deep inside a polystyrene-based polymer. Greater cross-linking within a polystyrene-based catalyst leads to tighter polymer chains and smaller channels up to the active site; this will generally decrease catalytic activity and will also influence selectivity. Selectivity depending on the size of olefinic substrates was demonstrated, the smaller olefin (ignoring solvation) being most rapidly hydrogenated. Polarities of the solvent, and hence of the substrate, also influence activity and selectivity. An increase in solvent polarity decreases the swelling of polystyrenes, leading to expected size effects, but also promotes diffusion of nonpolar olefins and impedes diffusion of polar olefins to the catalytic site. Selectivity may also result from the presence around the active site of groups from the polymer itself, analogous in principle to enzyme systems.

Considerable differences in reactivity for olefin hydrogenation have been observed for even a series of "similar" catalysts; e.g., for some rhodium(I) complexes on a phosphinated polystyrene, $\text{RhCl}_3 > \text{RhCl}_3 + \text{PPh}_3 > \text{RhCl}_3 + \text{PPh}_2 > \text{RhCl}_3 + \text{C}_2\text{H}_4 > \text{RhCl}(\text{PPh}_3)_3 > \text{RhCl}(\text{PPh}_2)_3$.

Clearly, considering the number of variable parameters, the matching of substrates and catalysts to give high selectivity is at this stage somewhat of an empirical art and perhaps mimics in this respect its twin subject, asymmetric hydrogenation (Section III); they were both born in 1968-1969.

The supported catalysts are generally less active than homogeneous ones because of the presence of inaccessible sites in the former. However, polystyrene-supported $\text{RhCl}(\text{PPh}_3)_3$ and $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$ (see Section II,B) do approach the activity of their homogeneous counterparts for hydrogenation of 4-vinylcyclohexene, 1,5-cyclooctadiene, and 1,5,9-cyclododecatriene (329); similarly supported $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ is more active under certain conditions than its homogeneous counterpart for the diene hydrogenations (330, 331). Improvement in the activity of phosphinated silica supported rhodium(I) catalysts for 1-hexene hydrogenation has been achieved by using a double carrier comprised of silica covered with a polyphenylsiloxane (332), and the activity of some chlorotriphenylphosphine complexes of rhodium(I), cobalt(II), nickel(II), and palladium(II) has been greatly enhanced by supporting them on phosphine-modified silica (333).

Deactivation of a homogeneous catalyst by dimerization can usefully be prevented by supporting the monomeric unit [note also that most multicenter catalysts require dissociation to an active monomeric form (1, p. 405; also Section VI)]. This concept has been used to maintain the hydrogenating activity of titanocene intermediates, which normally dimerize to inactive fulvalene complexes (334-336). Similarly maintained

is the activity of a $\text{Rh}_6(\text{CO})_{16}$ -polymeric amine catalyst that reduces the olefinic bond in α,β -unsaturated carbonyl and nitrile compounds by using carbon monoxide and water as a hydrogen source (see Section VI,C), the lower activity of the homogeneous $\text{Rh}_6(\text{CO})_{16}$ system being attributed to dimerization to a Rh_{12} species (337, 338). Metallic Rh_6 clusters, active for hydrogenation using H_2 , and formed by photolysis of supported $(\text{Ph}_2\text{P})\text{Rh}_6(\text{CO})_{15}$ species, are similarly prevented from aggregating (339). Interaction of polynuclear rhodium carbonyls with alumina in terms of their potential for catalytic activity has been studied (340). Other supported cluster systems are considered in Section VI.

The activity of a rhodium catalyst $(\text{poly-OPPh}_2)_2\text{Rh}(\text{CO})\text{Cl}$, incorporated into a polyphosphinite obtained from atactic poly(methallyl alcohol) (341) has been shown to be due the presence of metal (342). Other similar complexes with isotactic and syndiotactic poly(methallyl alcohol) were also inactive unless decomposition to metal occurred, and this was attributed to "polymer strain" caused by action of the rhodium as a cross-linking agent between the initially linear polymers (342). Polystyrene-supported $\text{Rh}(\text{NBD})(\text{phosphine})_2^+$ systems can show similar behavior (343). It should be noted that deposition of metal particles within or on polymers (e.g., by treatment of transition metal salt/polymer mixtures with borohydride) can yield highly active catalysts, and, for example, such systems using a nonporous methacrylate gel have potential for selective reductions in terms of a different extent of polymer swelling with different solvents (344, 345). Rhodium(I) centers supported on phosphinated poly(sulfonatohexadiyne) are reported to hydrogenate conjugated olefins and benzene (346), but the latter hydrogenation may be due to metallic rhodium, because inactivity toward benzene has been used as a criterion for the absence of metal (347), and the homogeneous analogs do not effect hydrogenation of aromatics (1, Chapter XI).

Electron spin resonance (ESR) signals, detected from phosphinated polystyrene-supported cationic rhodium catalysts both before and after use (for olefinic and ketonic substrates), have been attributed to the presence of rhodium(II) species (348). The extent of catalysis by such species generally is uncertain, although the activity of one system involving RhCl_3 /phosphinated polystyrene has been attributed to rhodium(II) (349). Rhodium(II) phosphine complexes have been stabilized by steric effects (350), which could pertain to the polymer; alternatively (351), disproportionation of rhodium(I) could lead to rhodium(II) [Eq. (61)]. The accompanying "isolated" metal atoms in this case offer a potential source of ESR signals as well as the catalysis.



A sequential cyclooligomerization of butadiene, followed by hydrogenation, has been accomplished by attaching two catalysts to the same polystyrene polymer or by using a mixture of two resins containing the individually anchored complexes; $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$ catalyzed the oligomerization, and $\text{RhCl}(\text{PPh}_3)_3$ or $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$ the hydrogenations (25, 352). The concept of sequential multistep reactions in the same reactor has been applied previously in enzyme immobilization studies (353).

The phenyl ring of a polystyrene resin has now been used to give an anchored tricarbonylchromium moiety, and the system is active, much like the analogous $(\text{arene})\text{Cr}(\text{CO})_3$ homogeneous catalysts (1, p. 50 and Section VIII), for selective hydrogenation of dienes to monoenes (354). Exchange of cations in the intracrystal space of a swelling layer lattice silicate has yielded ionically bonded Rh_4^{2+} and $\text{Rh}(\text{PPh}_3)_x^+$ olefin hydrogenation catalysts (347), which have been used previously in cationic exchange resins and in solution (355; also 1, p. 28). Other more recently reported work on supported ruthenium catalysts for alkene hydrogenation include the use of $[\text{RuCl}_2(\text{CO})_3]_2$ and $\eta^3\text{-C}_3\text{H}_5\text{RuCl}(\text{CO})_3$ [Section XI, Eq. (92)] with polyvinylpyridine, $\text{H}_3\text{Ru}(\text{CO})(\text{PPh}_3)_3$ with polyacrylic acid (356, 357), and the $\text{HRuX}(\text{PPh}_3)_3$, $[\text{HRu}(\text{PPh}_3)_3]_2\text{X}$ complexes (X = carboxylate) (Section II,A) on maleic anhydride/ethylene copolymers (358). Olefin and acetylene hydrogenations have been accomplished using palladium(II) on polymeric diphenylbenzylphosphine (359), and an anionic rhodium acetylacetonate complex on an anion exchange resin (360); data continue to appear on polystyrene-supported rhodium phosphine catalysts (361). The hydridorhodium(III) carborane catalyst mentioned later in Section XI has been supported on polystyrene (362).

The $[\text{RhCl}(\text{CO})_2]_2$ dimer immobilized on a cross-linked polystyrene containing pyrrolidine effects the same novel selectivity as the homogeneous analog in hydrogenation of α,β -unsaturated aldehydes to the unsaturated alcohols, Eq. (30) (162).

Nickel(II) phosphine complexes have been used to catalyze the borohydride reduction of the nitro group in aromatics; while the homogeneous $\text{NiCl}_2(\text{PPh}_2\text{R})_2$ catalysts (R = Ph or $-\text{CH}_2\text{Ph}$) gave a mixture of products (azoxy, azo, and amine compounds), the corresponding systems supported on polystyrene showed high selectivity for production of azoxy compounds (363).

In terms of chelating systems, nitrogen and oxygen donors (bipyridine, phenanthroline, crown ethers, etc.) have also been attached to polymer supports (364), as well as chelating phosphorus donors (see Section IV,B).

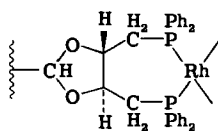
A major problem remaining in the supported catalyst area is the difficulty in obtaining detailed information about the structure of the metal complex at the active site (17). It is also difficult to determine whether during catalysis the active metal site remains bonded to the surface, or whether the active species is reversibly abstracted into the solution (effectively a homogeneous process). Both may occur (27). Indeed, as the length of a chain carrying the functional ligand increases, the system must pass through the ill-defined gray area between the extremes of heterogeneous and homogeneous catalysis.

B. Asymmetric Hydrogenations

Asymmetric hydrogenations catalyzed by supported transition metal complexes have included use of both chiral support materials (polyimines, polysaccharides, and polyalcohols), and bonded chiral phosphines, although there have been only a few reports in this area.

An early example (319) involved the use of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in poly(L-methylethylenimine) for hydrogenation of acetoacetate. This was also the first reported chiral ruthenium catalyst, and it is discussed in Section III,C, Eq. (60).

Use of benzene suspensions containing a neutral rhodium(I)-DIOP complex supported on a cross-linked polystyrene (50) (cf. 13 in Section III,A) for hydrogenation of α -ethylstyrene (to 1.5% ee) and methyl atropate (2.5% ee) was less effective than the homogeneous system, as the ethanol cosolvent required for substrate solubility caused a collapse of the resin (296).



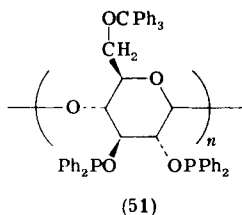
(50)

However, on a lightly cross-linked hydroxyethylmethacrylate/styrene polymer that swells in polar solvents (22, 365), or on a silica-gel support (366), catalyst performance matches that of the soluble one for the precursor amino acid substrates. A rhodium-DIOP analog has also been supported on a polymer containing pendent optically active alcohol sites [incidentally, formed via hydrosilylation and hydrolysis of a ketonic polymer component using an *in situ* rhodium(I)-DIOP catalyst]. The supported catalyst in alcohol again matched that of the soluble catalyst for

amino acid syntheses. In tetrahydrofuran (THF), the optical yields varied with the configuration of the alcohol groups, indicating that they play some role, but there was no asymmetric synergism or cooperative effects, and indeed the optical yields in this solvent were low (367).

Supported cationic rhodium(I) phosphine complexes, chiral at a menthyl moiety, effected hydrogenation of ketones, but the 2-butanol produced from methylethylketone was optically inactive (348). Polystyrene- or silica gel-supported DIOP systems, however, are particularly effective for production of optically active alcohols (up to 60% ee) via asymmetric hydrosilylation of ketones (10, 284, 296, 366, 368; see also Section III,A,4).

Synthesis of 2,3-O-bis(diphenylphosphino)-6-O-triphenylmethylcellulose (51), a cellulose-supported C-chiral diphosphinite analogous to the homogeneous counterpart (41) shown in Section III,A,1, has led to a rhodium(I) catalyst giving high stereoselectivity (77% ee) for a slow hydrogenation of 2-phenylbut-1-ene at 50 atm H_2 , but only a 17.5% optical yield with α -acetoamidocinnamic acid (369).



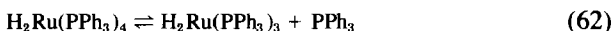
In contrast, the homogeneous DIOP system gave 33% ee with the butene and up to 79% ee with the olefinic acids.

V

MEMBRANE SYSTEMS, PHASE-TRANSFER CATALYSIS, MOLTEN SALT SYSTEMS

New approaches to catalyst recovery and reuse have considered the use of membrane systems permeable to reactants and products but not to catalysts (370). In an attempt to overcome the problem of inaccessibility of certain catalytic sites in supported polymers, some soluble rhodium(I), platinum(II), and palladium(II) complexes with noncross-linked phosphinated polystyrene have been used for olefin hydrogenation. The catalysts were quantitatively recovered by membrane filtration or by precipitation with hexane, but they were no more active than supported

analogs (371). Use of a membrane for selective removal of an involatile ligand, e.g., free phosphine in an equilibrium such as (62), seems an attractive way of increasing the concentration of an active catalyst species, in this case $\text{H}_2\text{Ru}(\text{PPh}_3)_3$ (372).



Ligands which allow catalysis in biphasic systems have been synthesized. Use of sulfonated triphenylphosphine allows formation of water-soluble *in situ* rhodium phosphine complexes which can, for example, catalyze hydrogenation of cyclohexene, present as a separate organic phase; removal of the hydrogenated organic layer leaves the catalyst solution ready for further reaction (373); addition of small amounts of cosolvents (alcohols, amides) greatly improved hydrogenation rates. Following the same principle, water-soluble olefins can be hydrogenated in an aqueous phase on shaking with benzene solutions of $\text{RhCl}(\text{PPh}_3)_3$ under H_2 (373). The general principles of phase-transfer catalysis can be found in reviews (328, 374, 375).

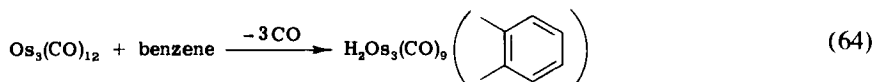
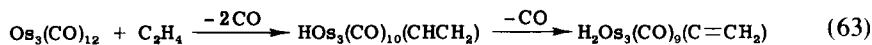
Use of molten salts as solvent allows easy separation of organic products by distillation (376), and in this way PtCl_2 with tetraalkylammonium salts of SnCl_3^- and GeCl_3^- has been used to selectively hydrogenate 1,5,9-cyclododecatriene to cyclododecene; the salts in this case act as both solvent and ligand (377). A molten salt medium has been used in a homogeneously catalyzed Fischer-Tropsch synthesis (see Section VI,B).

VI

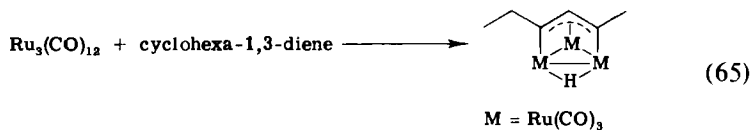
TRANSITION METAL CLUSTERS, INCLUDING DIMERS

Some comparisons between homogeneous and heterogeneous catalysts were considered in Section IV on supported catalyst systems, which in some ways span both areas. The study of a discrete molecular mononuclear homogeneous catalyst, in terms of its geometric and stereochemical features in the solid state and in solution, can be tackled using standard physical techniques. The catalyst can be studied on its own and during interaction with, for example, olefins and/or H_2 , and a great deal can be learned about detailed reaction mechanisms. Heterogeneous catalytic systems require a study of surfaces both in the absence and presence of the reacting molecules; low-energy electron diffraction (LEED) and Auger spectroscopy have been used principally, but these techniques (378, 379) are usually only applicable at low-pressure conditions, very different to those used in the catalysis.

Simply because of geometrical considerations, catalysis at a surface must involve more than one metal atom, and for this reason metal clusters have been considered as models of surfaces in chemisorption and heterogeneous catalysis (30, 31, 33, 380). The clusters can be solubilized and hence possess the experimental advantages of the mononuclear homogeneous catalyst. Limitations concerning the analogy between clusters and surfaces are realized, especially in terms of metal-metal bond energies, which are much weaker in the clusters, but the mode of bonding (e.g., terminal, bridging) of ligands such as hydrogen, carbon monoxide, and acetylenes in various carbonyl clusters has analogies in binding at surfaces (33). Equally important is the established mobility of ligands on clusters and of chemisorbed species on surfaces. Muetteterties' review (33) summarizes the studies, particularly involving $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$, that establish the ability of clusters to cleave C—H bonds [Eqs. (63) and (64)] and C—C bonds. Reaction (63) (381-383), for example, is considered analogous to ethylene chemisorption on metal surfaces. Reaction (64), in which the benzyldiene moiety becomes bonded to two osmium atoms, shows cleavage of two C—H bonds (384, 385).



Cleavage of C—H bonds is also well documented for mononuclear complexes (66-68, 147), and seems likely for dinuclear systems [(84, 386); also Section II,A, Eq. (7)]; but apart from some cyclopropane systems (387), cleavage of C—C bonds has not been demonstrated at mononuclear centers. Equation (65) shows such cleavage at a cluster center (388):

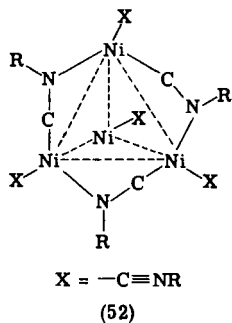


A. Hydrogenation of Organics

In terms of hydrogenation, solutions of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ reduce ethylene stoichiometrically, and the resulting unsaturated intermediate $\text{Os}_3(\text{CO})_{10}$ can oxidatively add H_2 , or further ethylene to give a hydridoalkenyl

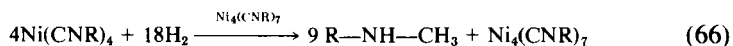
cluster [cf. Eq. (63)]. Other activated olefins, such as fumarate or maleate, react with $\text{H}_2\text{Os}_3(\text{CO})_{10}$ to give hydridoalkyl clusters, and these react with H_2 to liberate the saturated product with regeneration of $\text{H}_2\text{Os}_3(\text{CO})_{10}$. The system thus operates catalytically, and a hydride route via an $\text{H}_2\text{Os}_3(\text{CO})_{10}(\text{alkene})$ intermediate was favored (389).

The tetrahedral nickel isonitrile cluster $\text{Ni}_4(\text{CNR})_7$ (R = cyclohexyl or *t*-Bu) contains three bridging isonitrile ligands and a terminal one at each nickel (52); the bridging ligands are mobile on the cluster surface and a ligand dissociation step occurs (33, 390, 391).



The cluster catalyzes hydrogenation (20°C and 3 atm) of dialkyl- and diarylacetylenes to the *cis*-olefins via unsaturate routes, likely involving $\text{Ni}_4(\text{CNR})_6(\text{RC}\equiv\text{CR})$ and $\text{Ni}_4(\text{CNR})_4(\text{RC}\equiv\text{CR})_3$ (391, 392). The acetylenes in the latter complex bridge three nickel centers, and increase of the acetylenic carbon-carbon bond distance is considered to enhance reduction by hydrogen (392, 393).

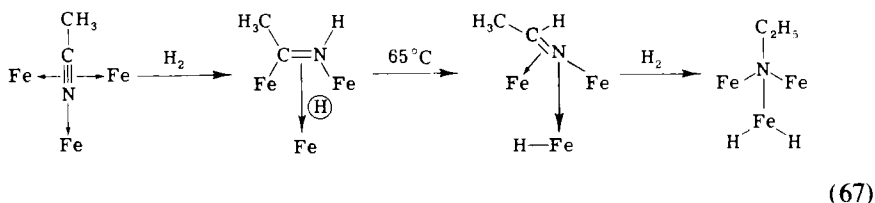
The *tert*-butyl cluster $\text{Ni}_4(\text{CNR})_7$ also catalyzed slowly the selective H_2 reduction of the isocyanide to *tert*-butylmethylamine (394). A problem arose in that the excess isocyanide resulted in formation of $\text{Ni}(\text{CNR})_4$, which is relatively inactive, but this was circumvented by using for the isocyanide source a "buffered" solution containing $\text{Ni}_4(\text{CNR})_7$ and $\text{Ni}(\text{CNR})_4$ in a 1:10 ratio:



Practical systems based on Eq. (66), but using $\text{Ni}(\text{COD})_2/\text{RNC}$ mixtures, were reported. Catalysis via $\text{Ni}(\text{CNR})_3$ or $\text{Ni}(\text{CNR})_2$ intermediates could not be completely ruled out in these cluster systems. The nickel isonitrile and acetylene clusters did not effect hydrogenation of the triple bond in nitrogen (394).

In terms of models for reduction of triple bonds, a series of isolated iron carbonyl clusters, which nicely show H-atom mobility, provides a

possible sequence for the reduction of $\text{C}\equiv\text{N}$ bond in acetonitrile (395):



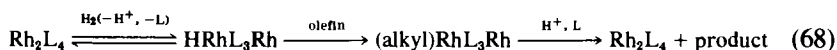
[Fe represents $\text{Fe}(\text{CO})_3$, and the three metal-metal bonds are not shown; $\textcircled{\text{H}}$ represents an H atom held on cluster face between iron atoms.]

In early reports on hydrogenations catalyzed by ruthenium carbonyl clusters, e.g., $\text{Ru}_3(\text{CO})_{12}$, $\text{Ru}_3(\text{CO})_{10}(\text{NO})_2$ (1, p. 99), the detailed nature of the active species was not elucidated, although dimeric species were favored in one case (396). More recent reports (397, 398) concerning hydrogenation of 1-pentyne catalyzed by $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ imply that a cluster, in which the acetylene replaces carbonyls, remains as the active catalyst. The $\text{Ru}_3(\text{CO})_{12}$, $\text{Os}_3(\text{CO})_{12}$, and $\text{Ir}_4(\text{CO})_{12}$ clusters are not very effective for olefin hydrogenations (399). Kinetic studies on hydrogenations using cluster carbonyls such as $\text{Rh}_4(\text{CO})_{12}$ and $\text{Co}_2(\text{CO})_8$ indicate that the catalysts are monomeric hydridocarbonyls (1, pp. 154, 262), although the activity in a $\text{Rh}_6(\text{CO})_{16}$ system has been attributed to the cluster (337, 338; Section IV, A). Although $\text{Co}_4(\text{CO})_{12}$ is inactive for hydrogenation of styrene, the mixed metal clusters $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ and $\text{Co}_3\text{Rh}(\text{CO})_{12}$ are reported to be active catalysts at low hydrogen pressures (400).

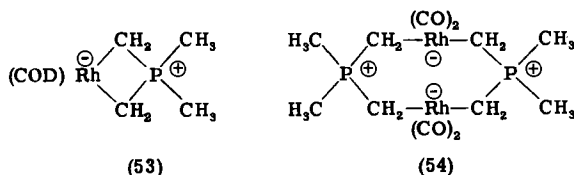
Hydrogenation of ethylene catalyzed by $\text{Pt}(\text{SnCl}_3)_5^{3-}$ has been studied mechanistically (401) and an unusual rate dependence on catalyst concentration, in which two maxima were observed, together with spectroscopic data, was interpreted in terms of monomeric and especially cluster Pt_6 catalysts. A cycloocta-1,5-diene complex, presumably $(\text{C}_8\text{H}_{12})_3\text{Pt}_3(\text{SnCl}_3)_2$ (402), is reported active for hydrogenation of olefins, acetylenes, and nitrobenzene (403). Some rhodium and iridium phosphite clusters $\{\text{HM}[\text{P}(\text{OR})_3]_2\}_n$ ($n = 2$ or 3) effect catalytic hydrogenation of hex-1-ene, but it is not known whether the clusters or monomers are the active species (404).

Detailed kinetic studies are essential to help establish that a multicenter complex is not dissociating to an active monomeric catalyst—as is usually the case (1, p. 405). An added problem in some of these ligand-deficient systems (394, 405) is to establish that the catalysis is homogeneous. Even when an active polynuclear system is confirmed, it is likely impossible to demonstrate unequivocally that reactivity does not occur at a single

site within the cluster! In the hydrogenation of olefins catalyzed by the dimeric rhodium(II) acetate $\text{Rh}_2(\text{OCOMe})_4$, only one metal center *within* the dimer is thought to be involved in a postulated hydride route (406):



Interestingly, oxidative addition of H_2 to the dimeric $[\text{Ir}(\mu\text{-SBu})(\text{CO})(\text{PPh}_3)]_2$ complex yields $[\text{HIr}(\mu\text{-SBu})(\text{CO})(\text{PPh}_3)]_2$ with one hydrogen atom bound to each iridium (407); this contrasts with the behavior of $[\text{RhCl}(\text{PPh}_3)_2]_2$ (1 in Section II,A). The clusters $\text{Ir}\{\text{M}[\text{P}(p\text{-tolyl})_2](\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\}_2^+$ ($\text{M} = \text{Fe}$ or Ru) reversibly bind one mole H_2 at ambient conditions (408), presumably at the iridium. The rhodium ylido complex shown in 53 catalyzes hydrogenation of simple olefins (409). The ylido ligand can also bridge two rhodium atoms (54), and it was hoped that the nonlabile character of the ylido ligands would lead to dimers of unusual catalytic behavior.



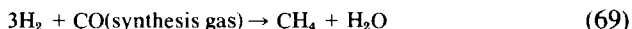
However, carbonylation of methyl iodide catalyzed by 54 likely involves monomeric species (409). The bridged-sulfide complex $\text{Rh}_2(\mu\text{-S})(\text{CO})_2(\text{DPM})_2$, where DPM is bis(diphenylphosphino)methane, also catalyzes olefin hydrogenation (410).

Clusters can undoubtedly be maintained on support materials. Besides a number of examples considered in Section IV, discrete nickel clusters, such as $\text{Ni}_3\text{Cp}_3(\text{CO})_2$, dispersed on silica, have been found active for hydrogenation of ethylene and benzene at ambient conditions (411). Attempts to prepare highly dispersed metal crystallites of controlled size are promising in terms of producing highly selective catalysts (412), and, for example, pyrolysis of $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ on silica gives $(\text{Pt}_3)_n$ aggregates which absorb H_2 (413). Production of naked clusters of single or mixed metal systems via photoaggregation of metal atomic species at low temperatures is an alternative and possibly even more promising approach (414, 415).

The potential of naked cluster ions (416), for example Bi_5^{3+} , for catalysis has been noted (33), but hydrogenations have not yet been reported.

B. Fischer-Tropsch Syntheses

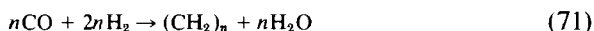
A search for alternative energy supplies has triggered efforts to develop efficient homogeneous catalysts for Fischer-Tropsch-type syntheses via hydrogenation of carbon monoxide, a likely future key material available, for example, through oxidation of coal (33, 327, 328, 417, 418). Metal cluster systems have been used in attempts to emulate the presently used heterogeneous catalysts. The important reactions are methanation,



methanol production,

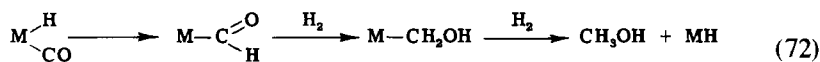


and production of paraffins, olefins and alcohols, for example,

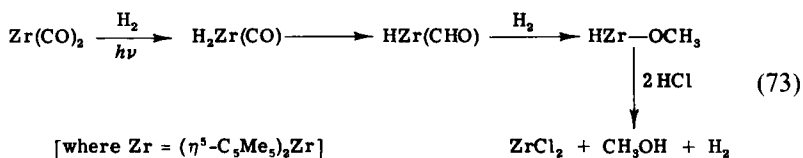


Patents by Union Carbide (419) describe the use of $\text{Rh}_6(\text{CO})_{16}$ and $\text{Rh}_{12}(\text{CO})_{30}^{2-}$ at extreme conditions (250°C, up to 3000 atm) for conversion of CO and H_2 to ethylene and propylene glycols and other products; a recent paper describes the systems as homogeneous (419a). $\text{Os}_3(\text{CO})_{12}$ and $\text{Ir}_4(\text{CO})_{12}$ catalyze homogeneously and specifically reaction (69) in toluene at 140°C and 1-3 atm but the rate is very slow, giving ~1% conversion in 4 days and a catalyst turnover of only 4 (420). Addition of trimethylphosphite or triphenylphosphine accelerates the iridium system somewhat, and in the latter case ethane and propane are also formed. A wide range of mononuclear catalysts were said to be inactive, although $\eta^3\text{-C}_3\text{H}_5\text{-Mn}(\text{CO})_4$ sometimes gave methane. The clusters were ineffective for N_2 reduction. Use of $\text{Ir}_4(\text{CO})_{12}$ in molten $\text{NaCl} \cdot 2\text{AlCl}_3$ under similar conditions converted synthesis gas much more efficiently to a mixture of alkanes, with ethane the primary reaction product (405). Carbonyl oxygen-aluminum interactions (M-C-O-Al) seem likely. Of a range of mononuclear and cluster carbonyls studied, only $\text{Ru}_3(\text{CO})_{12}$, $\text{Rh}_6(\text{CO})_{16}$, and $\text{Rh}_4(\text{CO})_{12}$ showed activity, but the systems were homogeneous only in the early stages of the reaction.

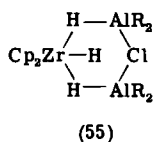
Borohydride reduction of cobalt(II) or nickel(II) chloride solutions containing RhCl_3 leads to the complexes $(\text{Co}_2\text{B})_{10}\text{RhH}_6$ and $(\text{Ni}_2\text{B})_{10}\text{RhH}_{15}$ which, when supported on glass wool, catalyze CO methanation with up to 60% conversion at 500°C, as well as gas phase hydrogenation of alkenes at 100°C (421).



The CO reductions generally could likely proceed through formyl intermediates, probably at a multinuclear site (420); hydride migration to a coordinated CO [e.g., as in the hypothetical scheme outlined in Eq. (72)] has not yet been observed, although metal formyl complexes have been synthesized via other methods (422–425). A π -bonded formyl also seems plausible (426), since π -bonded acyl groups have been demonstrated (427). A stoichiometric hydrogen reduction of CO to methanol under mild conditions via a bis(pentamethylcyclopentadienyl)zirconium complex is considered to go through a formyl intermediate (428, 429):



In related studies, Cp₂ZrCl₂ has been found to catalyze at room temperature an aluminum hydride (i-Bu₂AlH) reduction of CO to linear C₁–C₅ alcohols (430). The system involves reaction of complex 55 with CO, which precipitates the starting zirconium(IV) complex and leaves a yellow solution, that on hydrolysis yields the alcohols. Toluene solutions of Cp₂Ti(CO)₂ complex under H₂/CO effect Eq.(69), i.e., a homogeneous stoichiometric hydrogenation of carbon monoxide to methane (426).

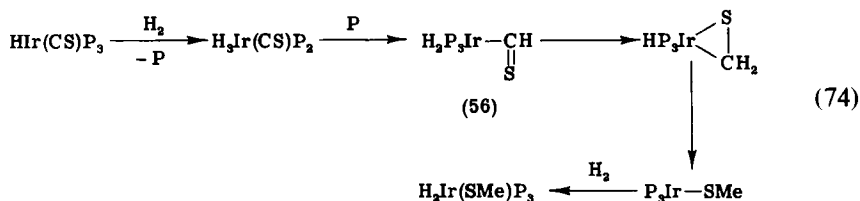


Use of D₂ yielded CD₄, and methane was formed from reaction of the complex with just H₂. The water produced in the reaction hydrolyzes the titanium complex to an inactive cluster Cp₆Ti₆O₈ containing bridging oxide ligands.

Of interest is the fact that the H₂ required for the reduction of formyl to methoxide in reaction (73) is thought (428, 429) to come from a second zirconium moiety, ZrH₂. The H₂ reduction to coordinated hydroxymethyl in Eq. (72) could presumably go via a mononuclear H₂M(CHO) intermediate, but such a reaction has not been demonstrated, nor has the final hydrogenolysis step via a presumed H₂M(CH₂OH) intermediate. Loss of water from this to give a carbene HM=CH₂ (431, 432) followed by further reactions with H₂ and CO, provides speculative pathways to higher hydrocarbons (417, 419a, 430, 433).

Hydride migration to a coordinated thiocarbonyl with formation of a

thioformyl has been demonstrated for an iridium complex (434), as has hydrogen reduction of coordinated thiocarbonyl to the methanethiolato ligand (435). Equation (74) shows the suggested pathway from reactant to isolated product via an intermediate thioformyl (56); such species have been synthesized by external attack of hydride on coordinated thiocarbonyl (435).



Fischer-Tropsch-type syntheses are more fully reviewed elsewhere in this volume (Chapter 2).

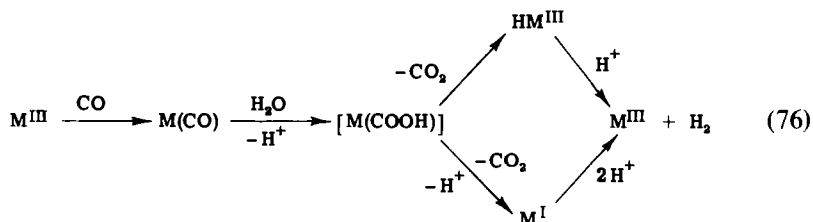
C. Water-Gas Shift Reaction

A further important industrial reaction is the water-gas shift reaction [Eq. (75)] which provides a way of increasing H_2 :CO ratios, or of producing pure H_2 . Pure H_2 is needed for ammonia synthesis, 2H_2 :1CO is needed for methanol synthesis, and 3H_2 :1CO is used for synthesis of substitute natural gas.



Several cluster carbonyls, including $\text{Ru}_3(\text{CO})_{12}$, $\text{Os}_3(\text{CO})_{12}$, $\text{Ir}_4(\text{CO})_{12}$, $\text{Rh}_6(\text{CO})_{16}$, and $[\text{Pt}_3(\text{CO})_6]_n^{2-}$, catalyze the reaction in basic solution (436, 437), although the mononuclear systems $\text{Fe}(\text{CO})_5$ in base (437), and $\text{Rh}(\text{CO})_2\text{I}_2^-$ in acid (438) are also effective.

The water oxidation of CO to CO_2 via a formate intermediate is well documented, and realistic pathways for reaction (75) at a single metal site are available (437, 438), for example:



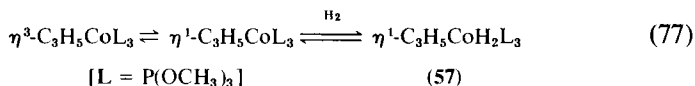
The CO/H₂O systems have been used to catalyze hydrogenation of olefins in Reppe hydroformylation (437), and a Rh₆(CO)₁₆-catalyzed system has been used to reduce the olefinic bond in α,β -unsaturated carbonyls and nitriles (337, 338, Section IV,A).

VII

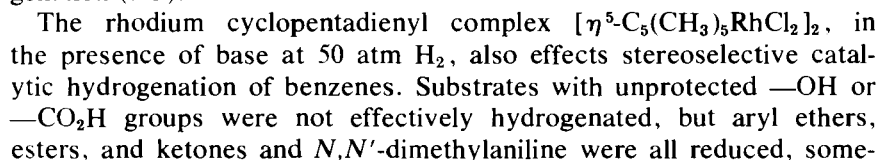
HYDROGENATION OF AROMATIC HYDROCARBONS

A number of catalysts are known to effect homogeneous hydrogenation of aromatic hydrocarbons, e.g., some oxidized rhodium complexes (1, p. 238), some rhodium π -complexes with phenyl carboxylates (1, p. 283), some Ziegler systems (1, p. 363), and Co₂(CO)₈ (1, p. 173). However, the catalysts in the first three systems are not well characterized, and the carbonyl systems require fairly severe hydroformylation conditions, although they are reasonably selective, possibly via radical pathways (Section II,C).

Muetterties and co-workers (439-443) have more recently found that some allylcobalt(I) complexes $\eta^3\text{-C}_3\text{H}_5\text{CoL}_3$ (L = tertiary phosphine or phosphite) catalyze hydrogenation of arenes to cyclohexanes at ambient conditions, although catalyst lifetimes were limited and turnover numbers low (~15 in 24 hours). With L = P(OCH₃)₃, C₆D₆ yielded solely *cis*-C₆D₆H₆, with no competing hydrogen exchange. Benzenes with substituent groups R, OR, CO₂R, CHO, COR, CH=CHR, C \equiv CR, and NR₂, were also reduced, sometimes accompanied by hydrogenation of the substituent group. Naphthalene, anthracene, and furan could also be fully hydrogenated. Interestingly, the catalysts show a slight selectivity for hydrogenation of arene when using benzene/cyclohexene or benzene/hexene mixtures as substrates, and because neither cyclohexene or cyclohexadiene was detected during hydrogenation of benzene, a mechanistic scheme was presented in which the C₆ moiety remained attached to the metal until a cyclohexyl species is formed:



Dissociation of phosphite from the dihydride (57), prior to reaction with the arene, is thought to give the nondetected intermediate $\eta^1\text{-C}_3\text{H}_5\text{CoH}_2\text{L}-\eta^4\text{-C}_6\text{H}_6$ (58), and then the sequence shown accounts for the stereoselectivity. NMR evidence was presented for 57, which also decomposes mainly according to reaction (78) in the absence of arene,



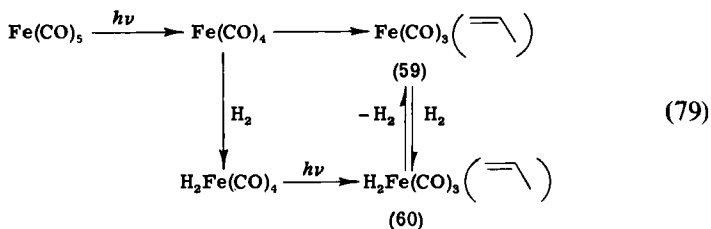
times accompanied by hydrogenolysis of the functional group (446). Permethyl arenes or cyclopentadienyl ligands are very resistant to hydrogenation and seem to be optimal ligands for hydrogenation of aromatics [note also the use of the silica-supported $\text{Ni}_3\text{Cp}_3(\text{CO})_2$ catalyst for hydrogenation of benzene (Section VI,A)].

Some bis(salicylaldehyde) complexes of cobalt(II), nickel(II), and copper(II), with or without lithium aluminum hydride, are said to catalyze hydrogenation of benzene and alkylbenzenes at $\sim 200^\circ\text{C}$, but the systems appear to be heterogeneous (447).

VIII PHOTOCATALYSIS

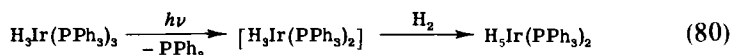
Photoassisted catalytic hydrogenation reactions invariably involve promoted loss of a ligand and generation of coordinatively unsaturated species. Examples in the literature are becoming increasingly common.

Olefin hydrogenation catalyzed by $\text{Fe}(\text{CO})_5$ normally requires somewhat severe conditions, typically 150°C and 10 atm H_2 (1, p. 64). With near-ultraviolet irradiation the carbonyl becomes effective at ambient conditions for hydrogenation (and isomerization) of olefins (448, 449). Photoinduced labilization of carbonyls is thought to give tricarbonyl species as the active catalysts, e.g.,



Successive hydrogen transfers within **60**, followed by coordination of olefin and then H_2 (an unsaturate route), constitute the catalytic cycle, while isomerization is effected through $\text{HFe}(\text{CO})_3(\pi\text{-allyl})$ formed from **59**. Loss of H_2 from **60** was also considered to be photoinduced, and several hydrides, including neutral and cationic dihydrides of iridium(III) (385, 450, 451), ruthenium(II) (452) and a bis(η -cyclopentadienyl)tungsten dihydride (453), have been shown to undergo such reductive elimination of hydrogen. Photoassisted oxidative addition of H_2 has also been dem-

onstrated [for example, see Eq. (80)] (451), and this could result in enhanced formation of hydrogenation catalysts.



Conjugated dienes yield mainly *cis*-monoenes by catalytic 1,4-hydrogen addition at ambient conditions using UV-irradiated solutions of $\text{Cr}(\text{CO})_6$ (454, 455) or $\text{Cr}(\text{CO})_3(\text{MeCN})_3$ (456); thermal systems using $(\text{arene})\text{Co}(\text{CO})_3$ require elevated temperatures and pressures (1, p. 50). Photoassisted systems using $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ are accompanied by isomerization of dienes and monoenes (455). More quantitative kinetic studies have appeared on the photoinduced hydrogenation of dienes using $\text{Cr}(\text{CO})_4(\text{norbornadiene})$ (457). The mechanism presented was similar to that outlined in Eq. (79), but involving a $\text{H}_2\text{Cr}(\text{CO})_4(\text{diene})$ intermediate. An isolated *trans,trans*-hexa-2,4-diene tetracarbonylchromium complex was also shown to be an intermediate in the hydrogenation of the diene using $\text{Cr}(\text{CO})_6$ (458). Addition of acetone to the $\text{Cr}(\text{CO})_6$ - or $\text{Cr}(\text{CO})_4(\text{diene})$ -photoinduced systems gave better activity and selectivity (459).

Other photoassisted hydrogenations induced by loss of a carbonyl ligand include the stoichiometric reduction of carbon monoxide using the zirconium and titanium cyclopentadienyl carbonyl complexes (426, 428, Section VI,B), and the use of a supported $\xi-(\text{Ph}_2\text{P})\text{Rh}_6(\text{CO})_{15}$ system (339, Section IV,A). An alternative source of the $\text{HRuCl}(\text{PPh}_3)_3$ catalyst (Section II,A) is via UV irradiation of $\text{HRuCl}(\text{CO})(\text{PPh}_3)_3$, although small amounts of $\text{HRuCl}(\text{CO})_2(\text{PPh}_3)_2$ result from reaction of the monocarbonyl with the photoreleased CO (452, 460). Photochemical loss of N_2 from $\text{H}_2\text{Fe}(\text{N}_2)(\text{PEtPh}_2)_3$ enhances its activity for hydrogenation (461, Section XI).

The activity of $\text{IrCl}(\text{CO})(\text{PR}_3)_2$ ($\text{R} = \text{Ph}, i\text{-Pr}, \text{C}_6\text{H}_{11}, \text{OPh}$) (see Section II,C), is markedly increased under UV irradiation, for example, by a factor of 40 for the triphenylphosphine complex in hydrogenation of acrylate; once formed, the intermediate [solvated $\text{IrCl}(\text{CO})(\text{PPh}_3)$ or $\text{IrCl}(\text{PPh}_3)_2$] remains active even in the dark (462-464). This photochemical system has also been used for selective hydrogenation of cyclic dienes to monoenes (463, 465, 466), and of 2-butyne-1,4-diol to 2-butene-1,4-diol (467). The activity of $\text{HRh}(\text{CO})(\text{PPh}_3)_3$, which decreases with time because of formation of the inactive $[\text{Rh}(\text{CO})(\text{PPh}_3)_2]_2$ dimer (1, p. 256), can be regenerated by UV irradiation (463, 468). The activity of $\text{RhCl}(\text{PPh}_3)_3$ for cyclooctene hydrogenation is increased by about three times on UV irradiation (469).

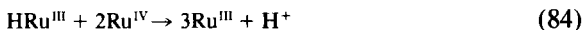
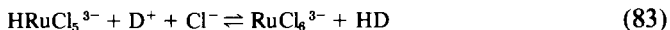
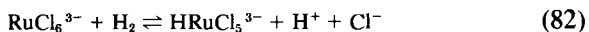
IX

HYDROGENASE SYSTEMS

There has been considerable effort in the last few years toward achieving an understanding of hydrogenase enzyme systems which have the ability to activate H_2 for exchange with water, para-ortho conversion, and reduction reactions when coupled to an electron carrier E such as NAD^+ , cytochrome c_3 , or ferredoxins (1, p. 396; 470-473). Reaction (81) can be catalyzed in either direction:

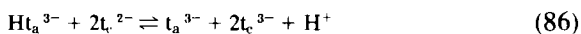


Advances in the area have resulted from isolation of purified enzymes, especially from *Clostridium pasteurianum* (474, 475), *Chromatium* (472, 476), and *Desulfovibrio vulgaris* (477), and from the development of quantitative extrusion of iron-sulfur cores from the active sites of hydrogenase and ferredoxins (473, 475, 478, 479). The enzyme systems have molecular weights in the range 60,000-70,000, although some preparations may consist of subunits (476). The extrusion work is based on a synthesis of analogs (480, 481) of the recognized types of active sites in iron-sulfur redox proteins (470, 478, 482), $Fe(S-Cys)_4^{2-}$, $Fe_2S_2^*(S-Cys)_4^{2-}$, and $Fe_4S_4^*(S-Cys)_4^{2-}$, where S^* represents sulfide and (S-Cys) represents cysteinylate. Treatment of the oxidized or reduced proteins with thiols extracts the intact iron-sulfur cores as the thiol derivatives, and these are compared (UV/VIS, ESR, Mossbauer, redox data) with the characterized synthetic analogs. With a clostridial hydrogenase containing 12Fe, 12S, and 12Cys, the only extrusion product was $Fe_4S_4(SPh)_4^{2-}$, and so the enzyme preparation is thought to contain just three $Fe_4S_4^*(S-Cys)_4$ sites (479). Absorption spectra of the oxidized forms of the three enzyme preparations noted above are quite similar, indicating that all probably contain Fe_4 sites (473).



Knowledge of the active site allows for speculation on the mechanism of H_2 - D_2O exchange which these Fe_4 systems catalyze (473, 483). Ruthenium(III) systems catalyze such an exchange via a ruthenium(III) hydride intermediate (1, p. 73; Section II,A), as exemplified in reactions (82) and (83), and iron hydrides must be involved in the hydrogenase systems. Ruthenium(III) also catalyzes the H_2 reduction of ruthenium(IV) via reaction (82), followed by reaction (84) (3), and using these ruthenium systems as models, a very tentative scheme has been proposed (473) for

a hydrogenase-catalyzed H_2 reduction of a ferredoxin electron carrier. [In reactions (85)-(88), t = an Fe_4 site; a is the active catalyst center; and c is an electron-transfer center coupled to the endogenous 8-Fe ferredoxin electron carrier, Fd.]



Reactions (85) and (86) could occur within the enzyme and result in H_2 uptake or evolution, catalyzed (or autocatalyzed, as in the H_2 reduction of Ru^{IV}) by t_a^{3-} . Reaction (88) is the coupling reaction which with reaction (87) yields net reactions such as (81). The model is an attractive one and can be tested using the synthetic analogs; the oxidation level of t_a remains to be established (473).

A coupling of clostridial hydrogenase to photosynthetic systems can produce H_2 using water as the electron donor, and this system has been proposed as a basis for utilization of solar energy (484, 485) or biochemical hydrogen-oxygen fuel cells (486), but a problem is the sensitivity of the hydrogenase to oxygen (471). The air stability, however, is increased by immobilizing the enzyme on glass beads, although enzyme activity is markedly reduced (486, 487).

A better understanding of hydrogenase systems will also aid in improving the efficiency of nitrogenases in biological nitrogen fixation (488). Metabolic energy in the form of ATP and reducing power is wasted by nitrogenase in that a competing reaction to N_2 reduction is the reduction of protons to H_2 , which is evolved at least in systems tested *in vitro*. The *in vivo* systems are complicated by the presence of hydrogenases, and it has been shown recently that the aerobic azotobacter enzyme does produce H_2 , but this is reoxidized by hydrogenase to give additional reducing power and the gas is not evolved (489). Anaerobic nitrogenases (*Clostridium pasteurianum*) contain hydrogenases that evolve H_2 , and are thus less efficient for nitrogen fixation (490).

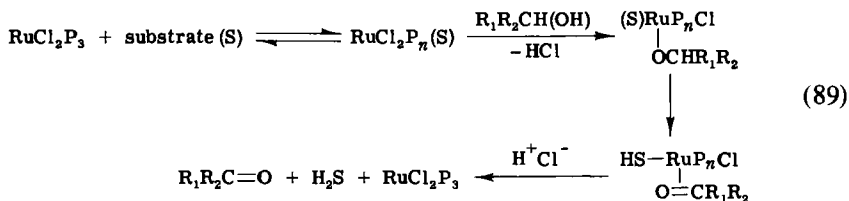
X

HYDROGEN TRANSFER FROM SOLVENTS

Considerable interest remains in catalyzed hydrogen-transfer reactions using as donor solvents alcohols, glycols, aldehydes, amides, acids, ethers, cyclic amines, and even aromatic hydrocarbons such as alkylben-

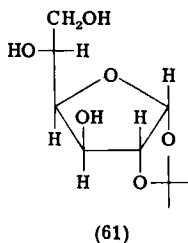
zenes and indane. Complexes that have been widely used are $\text{RhCl}(\text{PPh}_3)_3$ (491-493), $\text{HRh}(\text{PPh}_3)_4$ (494), $\text{RuCl}_2(\text{PPh}_3)_3$ (495-497), and $\text{H}_2\text{Ru}(\text{PPh}_3)_4$ (498-500). Two general reviews appeared in 1974 (501, 502).

Mechanisms, exemplified by alcohol as donor (493, 496), usually invoke coordination of the substrate (olefins, saturated and unsaturated ketones, and aldehydes), then coordination of the alcohol and formation of a metal alkoxide, followed by β -hydrogen transfer from the alkoxide and release of product via protonolysis:



Details of the various steps which will depend on the substrates and donors involved, are usually not well understood. Prior coordination of the donor followed by that of the substrate, equivalent to a hydride route (Section II,A), is also possible (494, 496). Formation of intermediate dihydrides from a donor (e.g., from an alcohol via oxidative addition to give a hydrido-alkoxide, and then β -hydrogen transfer) has also been invoked (491, 492, 496, 499, 500); in mechanistic terms, the hydrogenations then become equivalent to using molecular hydrogen for the reductions. The β -hydrogen transfer step is usually considered rate-determining (494, 496).

Use of $\text{RuCl}_2(\text{PPh}_3)_3$ with a glucofuranose derivative (61) as donor solvent leads to asymmetric hydrogenation of prochiral α,β -unsaturated ketones to the saturated ketones, with up to 34% ee in the case of a cyclohexene-3-one (497).

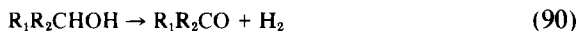


This appears to be the first asymmetric hydrogenation using a solvent as the hydrogen source. Closely related to this is the use of the ruthenium(II) catalysts $\text{Ru}_2\text{Cl}_4(\text{DIOP})_3$ (Section III,B) or $\text{RuCl}_2\text{P}_3^*$, where P^* is a chiral

phosphine P^*MePhR ($R = o$ - or p -anisyl, benzyl, propyl) or a neomenthyl(diphenyl)phosphine, for hydrogenation of activated olefins using racemic alcohols such as 1-phenylethanol (503-505). The process gives rise to an interesting enantioselective dehydrogenation of the alcohols, the optical purity of the remaining alcohol increasing with conversion to acetophenone [cf. Eq. (89); $R_1 = Ph$, $R_2 = CH_3$]. The maximum optical induction noted was 4.8% ee for the phenylethanol, using the neomenthyl phosphine system with benzalacetophenone $PhCH=CHCOPh$ as substrate. Optical yields were lower in the absence of hydrogen-acceptor substrates (504). An *in situ* rhodium(I) catalyst has also been used with the neomenthyl phosphine (506).

Full details have now appeared on the use of iridium(III)-sulfoxide complexes for catalytic hydrogen transfer from alcohols, a reaction which is particularly useful for stereoselective reduction of cyclic ketones (507, 508). The complexes *trans*- $Mo(N_2)_2(diphos)_2$ and $H_4Mo(diphos)_2$ have now been reported to hydrogenate ketones using secondary alcohols as the hydrogen donor (509), and salts such as $RhCl_3$ and $PdBr_2$ can reduce aromatic nitro compounds to the corresponding amines using other aromatic amines (e.g., indoline) as hydrogen donor (510).

Kinetic data have appeared on the decomposition of formic acid to hydrogen and carbon dioxide, catalyzed by iridium and rhodium phosphine complexes (511); hydride transfer to the metal from a coordinated formate group was considered rate-determining. Closely related is the dehydrogenation of alcohols [Eq. (90)] using the ruthenium(II) and osmium(II) carboxylate complexes $M(OCOR)_2(CO)(PPh_3)_2$ ($R = CF_3$, C_2F_5 , C_6H_5) (512). The mechanism involves initial alkoxide formation followed by β -hydrogen elimination to give the monohydrides $HM(OCOR)(CO)(PPh_3)_2$ and protonolysis to give H_2 and regeneration of catalyst [cf. Eq. (89)]. The detailed stereochemistry of the intermediates, which depends very much on the lability of the carboxylate ligand (including bidentate to monodentate equilibria), was elucidated.



XI

MISCELLANEOUS NEW CATALYSTS

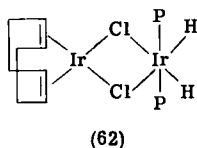
This section essentially catalogs some of the "newer" catalyst systems that have not been considered in the previous sections. A number of the catalysts are certainly derived from more established ones (e.g., use of chelated aminophosphine ligand instead of two monodentate phosphines

in analogs of Vaska's compound—see the first example), but they appear more innovative than those reviewed in Section II.

Complexes containing chelated aminophosphines $\text{IrCl}(\text{CO})(\text{PN})$, where PN is *o*-(diphenylphosphino)-*N,N*-dimethylaniline, or the dimethylbenzylamine analog, are somewhat more active than $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ for hex-1-ene hydrogenation (513). The rhodium(I) complexes $\text{RhCl}(\text{CO})(\text{PN})$, $\text{RhCl}(\text{PN})_2$, and $\text{Rh}(\text{PN})_2^+$ are not effective catalysts, although an acetylacetonate compound formulated $\text{Rh}(\text{C}_5\text{H}_8\text{O}_2)(\text{PN})$ was said to be active (514, 515). *In situ* rhodium(I) catalysts containing 2-aminopyridines are said to be more active than $\text{RhCl}(\text{PPh}_3)_3$ or $\text{HRuCl}(\text{PPh}_3)_3$ for hydrogenation of olefins (516). Complexes of the type $\text{M}(\text{N}-\text{N})(\text{diene})^+$ [where N—N is 2,2'-bipyridine or 1,10-phenanthrolines, and M = Rh or Ir], or a precursor rhodium(III) complex *cis*- $\text{Rh}(\text{bipy})_2\text{Cl}_2^+$, provide catalysts for hydrogenation of olefins or ketones under mild conditions in alkaline methanol (517, 518). The catalysis most likely occurs via hydride routes, because the complexes with 1,5-hexadiene show the same reactivity toward H_2 as the analogous Osborn phosphine complexes [see Eqs. (23) and (24), Section II,B,1]. The bisbipyridyl complex leads to $\text{Rh}(\text{bipy})_2^+$ which shows an unusual preference to hydrogenate a ketone rather than an olefin (518). Use of optically active chelating Schiff bases as the N—N ligand should permit asymmetric catalysis.

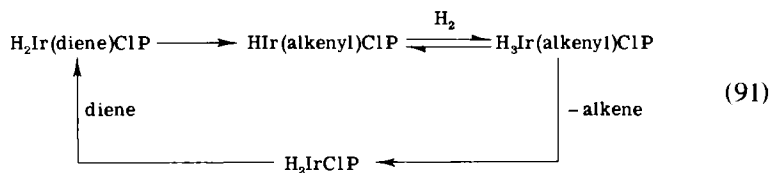
Hydrogenation of the 2-methylallyl group in the complex $\eta^3\text{-C}_4\text{H}_7\text{RhCl}_2$ in the presence of phosphines, sulfides, and amines, generates a range of *in situ* catalysts for olefin hydrogenation (519, 520); the most active were the isolated $\text{HRhCl}(\text{diphos})_2^+$ and $\text{RhCl}_2(\text{diphos})$ complexes. The rhodium(I) π -allyl $\eta^3\text{-C}_3\text{H}_5\text{Rh}(\text{PPh}_3)_2$ is similarly active (521), although a trifluorophosphine complex $\eta^3\text{-C}_3\text{H}_5\text{Rh}(\text{PF}_3)_3$ with H_2 yields propylene and inactive $\text{HRh}(\text{PF}_3)_4$ (522). Analogous to the $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ complex (1, p. 250), the trifluorophosphine complex $\text{HRh}(\text{PF}_3)(\text{PPh}_3)_3$ effects catalytic hydrogenation of terminal olefins (523). The cobalt analog (524) and the bisfluorophosphine species $\text{HRh}(\text{PF}_3)_2(\text{PPh}_3)_2$ are inactive (523).

The cyclooctadiene complex $\text{H}_2\text{Ir}_2\text{Cl}_2(1,5\text{-C}_8\text{H}_{12})(\text{PPh}_3)_2$, believed to have structure 62, catalyzes the hydrogenation of 1,5- and 1,4-cyclooctadienes to cyclooctene (525, 526).

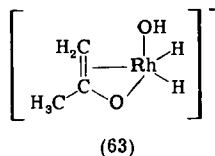


The major catalytic route was thought to involve a monomeric dihydride

intermediate, formed from **62** with excess diene:



In the presence of strong alkali, the rhodium analog of **62**, or $\text{RhCl}(\text{C}_8\text{H}_{12})\text{PPh}_3$, hydrogenates aliphatic ketones at 1 atm and 20°C, and after treatment with borohydride the systems similarly reduce aromatic ketones to the alcohols (526). Deuterium exchange data for acetone reduction were interpreted in terms of hydrogen transfer within a mono-nuclear hydroxy complex containing substrate bound in the enol form (**63**).

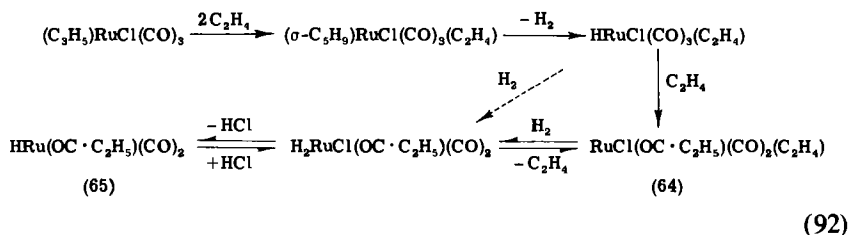


Incorporation of rhodium triphenylphosphine moieties into carboranes has led to $\text{HRh}(\text{C}_2\text{B}_9\text{H}_{11})(\text{PPh}_3)_2$ complexes, which are formally hydridorhodium(III) dicarbollides and which catalyze olefin hydrogenation under mild conditions (527). Iridium and ruthenium analogs are also known, including complexes with carboranylphosphine ligands, e.g., $\text{HRuCl}(\text{PPh}_3)[1\text{-P}(\text{CH}_3)_2\text{-1,2-C}_2\text{B}_{10}\text{H}_{11}]_2$ (527-530).

The rhodium allyl complex $(\eta^3\text{-C}_3\text{H}_5)\text{Rh}[\text{P}(\text{OMe})_3]_3$ catalyzes olefin hydrogenation but, unlike the cobalt analog (see Section VII), is inactive toward arenes because of the ease of cleavage of the Rh-allyl bond under H_2 (to give propane); the active catalyst is therefore considered to be $\text{HRh}[\text{P}(\text{OMe})_3]_n$ (531). Hydrogenation of the cobalt complex $\eta^3\text{-C}_3\text{H}_5\text{Co}[\text{P}(\text{O-i-C}_3\text{H}_7)_3]_3$ yields propene and the trihydride $\text{H}_3\text{Co}[\text{P}(\text{O-i-C}_3\text{H}_7)_3]_3$, which is an active catalyst for hydrogenation of olefins and the olefinic bond in α,β -unsaturated ketones and amides (532).

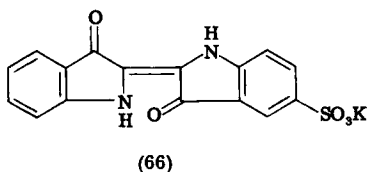
The ruthenium allyl $\eta^3\text{-C}_3\text{H}_5\text{RuCl}(\text{CO})_3$ catalyzes hydrogenation of terminal, internal, and cyclic alkenes, and of saturated aldehydes and ketones to alcohols under elevated conditions (100°C, 20 atm H_2) (533). The complex itself reacts with H_2 to give catalytically inactive polynuclear "alkyloxycarbene" derivatives, e.g., $[\text{RuCl}(\text{OC-C}_3\text{H}_7)(\text{CO})_2]_n$ and $[\text{RuCl}(\text{CO})_3]_2$, arising by hydrogenation of the allyl group together with

CO insertion reactions. The catalytic hydrogenation mechanism presented was based on detection of species **64** and HCl during hydrogenation of ethylene, Eq. (92). Species **65** then catalyzes the reaction by pathways outlined in Eq. (5).



Some π -allylmanganese(I) tetracarbonyl complexes, partly substituted by phosphites or phosphines, are apparently active for olefin hydrogenation (534).

The rhodium complexes formulated $\text{RhCl}_2(\text{HL})$ or $(\text{RhCl}_2)_2\text{L}$, where H_2L is indigo sulfonic acid (**66**), effect hydrogenation of olefins; the ligand is thought to coordinate through the carbonyl and ring nitrogen (535).



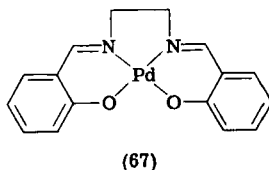
Solutions of $\text{HCo}(\text{N}_2)(\text{PPh}_3)_3$ are reduced by naphthalenide to give a binuclear species that catalyzes hydrogenation of olefins (536). The hydrogen in $\text{H}_2\text{Fe}(\text{N}_2)(\text{PEtPh}_2)_3$ may be used for stoichiometric hydrogenation of monoenes or dienes, and catalytic systems may also be established via hydride routes, the N_2 being lost during substrate coordination (461, 537).

Borohydride reduction of NiCl_2 in dimethylformamide or dimethylacetamide leads to very active catalysts, thought to be homogeneous, for hydrogenation of monoolefins, unsaturated fats, cyclic dienes to monoenes, and saturated aldehydes and ketones (165, 538, 539). Cobaltous chloride systems have also been used (540).

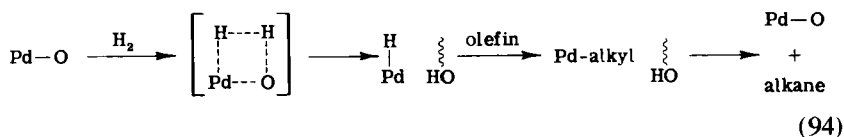
Use of copper(I) and silver(I) salts in ethylenediamine solution provides a method for catalytic H_2 reduction of nitroalkanes to oximes (541):



Palladium(II) and nickel(II) Schiff-base complexes such as **67** catalyze hydrogenation of 1-hexene in dimethylformamide at ambient conditions (542).



Kinetic data were interpreted in terms of a mechanism in which initial heterolytic cleavage of H_2 involved the basic O^- ligand; coordination of olefin at the generated free equatorial site, followed by insertion to give alkyl and then protonation of the Pd-alkyl bond by the phenolic OH group, completes the catalytic cycle:



Rates of hydrogenation (and hydrogen exchange in C_2H_5OD) passed through a maximum on varying pH; this behavior is typical of hydrogenases, also considered to involve heterolytic cleavage of H_2 (1, p. 396), and reactions akin to (94) were thought plausible for the enzyme systems, the required basic site being an anion of a chelated ligand. The nature of the active sites in some hydrogenases has been ascertained (Section IX).

Hydrogenation of aryldiazenido ($-N=NAr-$) complexes of transition metals remains of interest as they are considered models for nitrogenases (543). Reduction by H_2 to arylhydrazines, or ammonia and aniline, is possible depending on the complex used, and whether or not a heterogeneous catalyst is needed. The literature has recently been summarized (543). Systems which themselves activate the H_2 and transfer it to the azo moiety to give arylhydrazines, in the absence of a heterogeneous catalyst, include $Pt(BF_4)(NNAr)(PPh_3)_2$ (543, 544), $[Pt(NNH)(PPh_3)_2]_2^{2+}$ (545), $RhCl_2(NNAr)(PPh_3)_2$, and $RhCl_3(HNNAr)(PPh_3)_2$ (546, 547). The first-mentioned platinum complex is probably dimeric $[Pt(NNAr)(PPh_3)_2]_2(BF_4)_2$ with bridging $NNAr$ groups, but solvated monomeric species were considered reactive toward H_2 (543). The cationic complexes $Pt(NNAr)(PPh_3)_3^+$ and $Pt(HNNAr)(PPh_3)_3^{2+}$ react with hydrogen to yield $HPt(PPh_3)_3^+$ with evolution of nitrogen (548).

XII

SUMMARY

It should be clear from this review that interest remains high in hydrogenation reactions catalyzed by transition metal complexes, with the general aim of developing catalysts for selective hydrogenation under mild conditions. Olefin hydrogenations, for example, are important industrial processes, and selectivity is critical to the success of such processes. Greater product selectivity has an important impact on energy and resource utilization in terms of reduced process energy requirements for product separation and purification, and in terms of low-value by-products.

The advances in asymmetric hydrogenation—a stereospecific selectivity—have been notable, and an understanding of the detailed pathways is just beginning to emerge, although much remains to be done, and matching of substrates with the most suitable chiral catalyst still remains a fairly empirical art. The intensive studies on the nonchiral $\text{RhCl}(\text{PPh}_3)_3$ system (see Section II,A), and the cationic rhodium phosphine catalysts (see Section II,B,1) together with their iridium analogs (see Section II,C), demonstrate the quite remarkable degree of understanding that can be attained for a homogeneous hydrogenation catalyst at the molecular level. Enantiomeric products are used widely in the pharmaceutical industry and as food additives, and the production of either the natural or non-natural amino acids is at least one advantage shown by the organometallic catalysts (see Section III) compared to enzyme systems. The incorporation of an effective rhodium catalyst into a protein begins perhaps to bring closer together analogies between the two areas. Interest is growing in chiral catalysts based on less expensive metals, such as cobalt (see Sections III,B and III,C), and a wider range of chiral ligands, including naturally occurring ones, is being exploited (see Section III,C).

Catalysts for selective reduction of monoenes (usually based on increasing substitution at the double bond), polyenes to monoenes, and acetylenes to monoenes, are now easy to find (1, and this chapter). Catalysts that effect mild hydrogenation of the carbonyl group are becoming more common, and newer ones, include, for example, $\text{RhCl}(\text{C}_8\text{H}_{12})(\text{PPh}_3)$ (see Section XI) and cobaloximes (see Section III,C), as well as cationic rhodium complexes with nitrogen donors (see Section XI), which are based on the earlier phosphine analogs (see Section II,B,1). The well-known $\text{RuCl}_2(\text{PPh}_3)_3$ complex has now been shown to be useful for carbonyl reductions (see Section II,A). Effective asymmetric hydrogenation of ketones to optically active alcohols has been accomplished. Unusual and interesting selectivities discovered now include

preference for hydrogenation of (a) a ketone in ketone/olefin mixtures using $\text{Rh}(\text{bipy})_2^+$ (see Section XI); (b) an aromatic substrate in the presence of an olefin using allylcobalt(I) complexes (see Section VII); (c) an aldehyde in the presence of a ketone using $\text{RuCl}_2(\text{PPh}_3)_3$ (see Section II,A); (d) an α,β -unsaturated aldehyde to the unsaturated alcohol using a rhodium carbonyl amine complex (see Section II,B,2); (e) the more-substituted bond in a conjugated diene using $\text{CoBr}(\text{PPh}_3)_3$ (see Section II,C); and (f) dinitro aromatics to diamines via nitroamines using $\text{RuCl}_2(\text{PPh}_3)_3$ (see Section II,A). Hydrogenation of groups such as $\text{C}=\text{O}$, $\text{C}=\text{N}$, $-\text{NO}_2$, and $-\text{C}\equiv\text{N}$, especially in the presence of other sensitive functionalities, provides an area in which a great deal still needs to be done.

Progress is being made in the search for catalysts to hydrogenate aromatic systems (see Section VII). This area is likely to become increasingly important if coal, which contains polyaromatic compounds, is utilized more for production of petrochemicals. Stereospecific production of fully *cis*- $\text{C}_6\text{D}_6\text{H}_6$ from perdeuterobenzene has been reported; catalysts for selective hydrogenation of benzene to cyclohexene would be valuable.

Homogeneous catalysts have now been reported for hydrogenation of carbon monoxide, a combustion product of coal (see Section VI,B). More effective catalysts will undoubtedly be discovered in the near future. Polynuclear or, at least, binuclear sites are favored for reduction of the triple bond in carbon monoxide (see Section VI,B), and this together with the popular parallelism to heterogeneous systems, has renewed interest in metal clusters as catalysts (see Section VI). A nickel cluster is the first catalyst reported for mild (and selective) hydrogenation of the triple bond in isocyanide (see Section VI,A). The use of carbon monoxide and water as an alternative hydrogen source is reattracting interest (see Section VI,C).

Establishment of a free radical mechanism via H-atom transfer for hydrogenation using $\text{HMn}(\text{CO})_5$ (see Section II,D), and possibly also $\text{HCo}(\text{CO})_4$ (see Section II,C), suggests that more serious consideration for such mechanisms should be given for other hydridocarbonyl catalyst systems, and indeed for other homogeneous catalysts systems in general. The pentacyanocobaltate(II) catalyst can certainly operate by such a mechanism (see Section II,D).

The limitations of homogeneous systems have been recognized, and this has stimulated the development of supported catalysts to the extent that a few of them now reach activity levels comparable to those of the homogeneous counterparts. Highly selective catalysts have been reported, although the selectivity patterns are often different to those of a homogeneous analog (see Section IV). Supported asymmetric catalysts

are now beginning to attract attention (see Section IV,B). Alternative procedures for catalyst recovery, critical for the expensive but more active platinum metal systems, are being considered, and increased activity in the study of phase-transfer and membrane systems seems likely (see Section V). Hydrogenase enzyme systems may be considered as catalysts supported on a large semioordered polymer, and identification of the active site in such systems (see Section IX) will lead to improved model systems for this metalloenzyme.

There is clearly a growing interest in photocatalysis involving metal hydrides (see Section VIII) and hydrogenase systems (see Section IX), and the search for systems to utilize solar energy to dissociate water into its elements will undoubtedly intensify further efforts.

Finally, studies of hydrogenation catalysts have led to, and will continue to lead to, somewhat accidental but significant findings concerning activation (by cleavage) of C—H bonds [see Sections II,A; II,B,1; II,C; and VI], C—O bonds [Eqs. (18), (27), and (29)], and C—C bonds (Section VI).

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Homogeneous Catalysis of Hydrosilation by Transition Metals

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I

INTRODUCTION

The term hydrosilation can be used to describe an addition reaction in which compounds with one or more Si—H bonds add to any reagent. This review will describe marvelously numerous ways in which soluble complexes of transition metals act as catalysts for the hydrosilation of organic compounds, especially substituted and unsubstituted unsaturated hydrocarbons.

The simplest example might be the addition of trichlorosilane to ethylene:



When great care is taken to use pure reagents, 10^{-7} mole of chloroplatinic acid per mole of product causes this addition to occur rapidly near room temperature and to go to completion to give analytically pure ethyltrichlorosilane (100% yield based on trichlorosilane).

The addition is exothermic. Unfortunately, no experimental heats of hydrosilation have been published. For ethylene, the enthalpy of hydrogenation is $-\Delta H = 32.82$ kcal/mole (1). The enthalpy of hydrosilation is

estimated as $-\Delta H \approx 38$ kcal/mole (2). The enthalpy of hydrosilation for an olefin is likely to be about 5 kcal/mole greater than its heat of hydrogenation. The values are likely to vary with the structure of silanes as well as with the structure of the olefin, and someone ought to measure them. The enthalpies could be most useful to estimate Si—H bond values in many kinds of substituted silanes.

The first published examples of hydrosilation, which appeared about 30 years ago, noted that they were observed to proceed by free-radical mechanisms initiated thermally (about 300°C) (3), by acyl peroxides (4), by azonitriles (5), by ultraviolet light (6), or by γ radiation (7). The first hint that catalysts known to be effective for hydrogenation might also be effective for hydrosilation was found in a French patent (8) (1949) which stated that catalysts may be chosen from compounds and salts of the elements of Groups IIA, IVA, IB, and IIB of the periodic table and metals of Group VIII and certain of their salts. No example to demonstrate this was included in the patent.

The first explicit information appeared in 1953 in two U.S. patents (9) which showed that platinum black as well as platinized asbestos or silica were effective for addition of trichlorosilane to olefins. Platinum on charcoal was unusually active with trichlorosilane and acetylene, ethylene, butadiene, vinyl chloride, or vinylidene fluoride. Temperatures as low as 130°C were sometimes employed.

In 1957 (2) platonic, ruthenium, and iridium chlorides were shown to be catalysts leading to very rapid additions, sometimes below room temperature, of many kinds of SiH compounds. These findings initiated much activity, chiefly in industrial research laboratories, in several countries, because they indicated that the manufacture of new organosilicon monomers and many new silicone polymers and copolymers would become commercially practicable for the first time.

A thorough bibliography of hydrosilation up to 1965 was compiled in the Soviet Union by Lukevits and Voronkov (10). This work tabulates 2283 examples of the use of chloroplatinic acid, which they refer to as "Speier's catalyst," and 1554 examples describing mostly supported solid platinum catalysts but also describing PdCl_2 , IrCl_3 , $\text{Fe}(\text{CO})_5$, K_2PtCl_4 , RuCl_3 , colloidal Fe, NiCl_2 , and Pd, Ru, and Rh on supports.

Although many catalysts have now been found, some with special utility for certain reagents, most research is still devoted to the use of platinum and platinum compounds. No other catalysts have the wide utility and industrial efficiency of platinum. Special uses for platinum and other transition metals are disclosed in numerous patents. A competent review of these is beyond the scope of this chapter.

We will describe the effects of structure on reactivity during hydrosi-

lation in homogeneous solutions of platinum catalysts, and point out similarities and differences that have been observed with other catalysts. References only sufficient to document the data are chosen from journal articles, when possible. Earlier references can be found in the bibliographies of the articles that are cited. References to patents are given only when no journal articles dealing with the subject could be found. References to unpublished work from our laboratory are used as a last resort.

A consistently useful theory for a mechanism for homogeneous catalysis of hydrosilation has been expounded by Chalk and Harrod (*11-11d*). This theory is accepted, adapted, and relied on to give a qualitatively rational explanation for numerous data in the following discussions.

II

CHLOROPLATINIC ACID AS A HOMOGENEOUS CATALYST

A. *The Induction Period*

Commonly, when chloroplatinic acid is the source of the catalyst for hydrosilation and sometimes when salts of other metals are used, no effect is observed for some time after it has been added to a mixture of reagents. Then, rather suddenly a rapid reaction can ensue. This "induction period" can in some cases last for a relatively long time, even hours. An unpredictable induction period, followed by a very fast exothermic reaction, leads to difficult, sometimes dangerous situations when large amounts of reagents are employed.

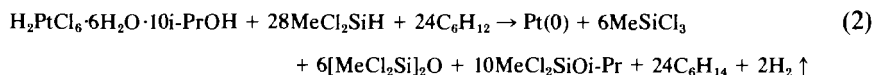
Nothing has been found in the published literature about what takes place during the induction period. We believe that an active catalytic species is formed during this period, and that its formation requires reduction of chloroplatinic acid, or of whatever transition metal salt or complex one uses.

Our experiences with chlorosilanes (*12*) indicate some of the processes that take place during an induction period. The experiences are synopsized as though they were obtained in one experiment. The results are in general accord with those described by Benkeser *et al.* (*13*), who studied the hydrosilation of styrene in ethylbenzene.

A very strong solution of chloroplatinic acid (about 50% in isopropanol) was stirred with an olefin to make a mixture containing the extremely high concentration of about 0.01 g-atom of Pt/mole of olefin. This is more than 100 times the amount one would use for hydrosilation. At room

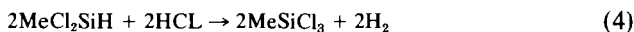
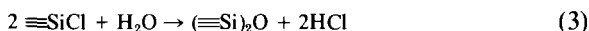
temperature, MeCl_2SiH was added in small increments. The first increments of MeCl_2SiH slowly produced slightly less than an equimolar amount of alkane and oxidized derivatives of MeCl_2SiH , chiefly MeSiCl_3 , $(\text{MeCl}_2\text{Si})_2\text{O}$, and $\text{MeCl}_2\text{SiOiPr}$, with minor amounts of other volatile siloxanes which were not identified.

If one were able to carry the reactions to completion with a large excess of olefin, chloroplatinic acid, and the chlorosilane, the reactions might be described by Eq. (2).

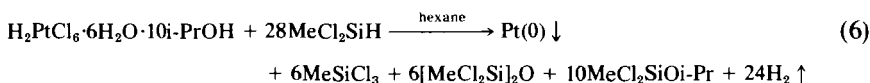


Protons originating from water and i-PrOH with H from MeCl_2SiH make alkanes in the quantity that was detected.

Experiments of this kind cannot prove that H_2PtCl_6 was reduced. H_2PtCl_6 could have acted as a catalyst for several alternate reactions, such as:



In hexane the suggested equation might be:



The amount of $\text{Pt}(0)$ required by Eq. (6) precipitated from hexane after several days. All the MeCl_2SiH was consumed, and products shown in Eq. (6) were the principal ones. Hydrogen chloride was carried from the system with hydrogen, so a complete material balance was not achieved. The siloxanes contained units such as $\text{MeHClSiO}_{1/2}$. However, Eq. (6) approximately described the reduction of chloroplatinic acid by MeCl_2SiH .

Experiments of this type in any olefin, even one such as cyclohexene which is exceedingly difficult to hydrosilate, produced optically clear solutions with no detectable precipitation of $\text{Pt}(0)$. Such solutions are usually yellow and stable indefinitely at room temperature. If they are warmed to about $80^\circ\text{--}100^\circ\text{C}$ they darken, turn brown, and become colloidal dispersions of $\text{Pt}(0)$. Platinum in the brown dispersions precipitates as a fine powder, sometimes in a few days at room temperature, sometimes in a few weeks. Catalytic activity was obviously reduced or completely lost by such solutions after they turned brown. A clear solution

in any olefin added to a solution of an Si—H compound in an olefin caused hydrosilation with no induction period. From this we conclude that clear solutions contain soluble platinum species, stabilized and solubilized by an olefin. To form this species the platinum was reduced to a state no higher than 2+, and very probably to the zero-valent state. Every effort to prove the structure of the soluble complex was frustrated.

The reactions of Eq. (2) could not be carried to completion in a reactive olefin such as 1-hexene. After several increments of MeCl_2SiH had been added to the mixture, succeeding increments were mostly consumed to form $n\text{-C}_6\text{H}_{13}\text{MeSiCl}_2$. When this product appeared in the solution, gas-liquid chromatography (GLC) showed that hexene in the solution was no longer only 1-hexene but a mixture of isomers which contained mostly 2- and 3-hexene, in both cis and trans conformations.

Harrod and Chalk (*11d*) observed that dichlorobisethylene- μ,μ' -dichloroplatinum(II) isomerized 1-hexene in the presence of nucleophilic mutual solvents. Similar isomerizations were observed with all complexes of Pt(II), Pd(II), Rh(III), and Ir(III). No isomerization was observed with chloro and carboxylate complexes of Fe(III), Co(II), Ni(II), and Ru(III).

Chalk and Harrod (*11a*) compared the above ethylene Pt(II) complex with chloroplatinic acid for hydrosilation, and found that each gave essentially the same results in terms of rate, yields, and products. Platinum(II) complexes and rhodium(I) complexes were very much alike in their behavior. No system was found in which a palladium-olefin complex brought about hydrosilation. In most systems the palladium complex was very rapidly reduced to the metal.

With excess 1-hexene at reflux under nitrogen with $10^{-6} M$ Pt(II), $(\text{MeO})_3\text{SiH}$ and $(\text{EtO})_3\text{SiH}$ added rapidly to completion without isomerization of 1-hexene. With Cl_3SiH , EtCl_2SiH , and PhCl_2SiH , hydrosilation proceeded less rapidly but went to completion with concurrent isomerization of excess olefin. With Et_3SiH , $(\text{PhCH}_2)_3\text{SiH}$, or Ph_3SiH , hydrosilation proceeded rapidly at first with isomerization of olefin, but the rates soon fell to zero and gave less than 20% of addition products. The mixtures turned brown from the moment the silane contacted the catalyst. This last class of silanes gave high yields of products if the mixtures were not permitted to rise above room temperature (*11a*).

B. The Catalytic Species

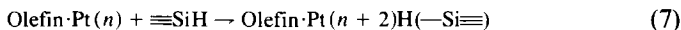
No direct proof exists for the structure of the species which are the catalysts during hydrosilation. A compelling amount of data is ration-

alized, at least qualitatively, if one accepts as a working hypothesis that the species is a soluble complex which contains at least one metal atom, M, complexed with at least one stabilizing olefin ligand, and substituted by a $-\text{Si}\equiv\text{C}^-$ group and H^- ; thus, olefin $\cdot\text{MH}(-\text{Si}\equiv\text{C})$.

A recent review in *Advances in Organometallic Chemistry* (14) described the synthesis and reactions of a great many stable complexes of transition metals that contain Si—M bonds, in which M is Ti, Zr, Hf, Cr, Mo, W, Mn, Re, Fe, Ru, Co, Ir, Ni, or Pt. Some of these are hydrides, Si—M—H, and nearly all contain π -acceptor ligands to stabilize them.

The mechanism of hydrosilation can be rationalized as described by Chalk and Harrod (11-11d). In this view, all the chemical changes take place within the coordination sphere of a transition metal. Other reactions of unsaturated molecules are explained in much the same way. Hydrogenation, the oxo-process, and the Ziegler process are important examples.

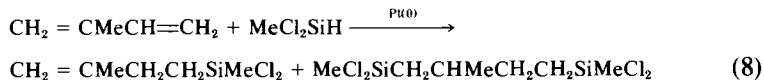
With a platinum compound as the source of the catalyst, the process can be viewed as beginning by oxidative addition of SiH to a low-valence form of Pt stabilized by olefin:



If $n = 2$, one set of ligands can be accommodated. If $n = 0$, two sets lead to $(\text{olefin})_2\cdot\text{PtH}_2(-\text{Si}\equiv)_2$. Both cases have Pt(IV) in the catalytic species. Perhaps this is not a necessary condition for catalysis, but it seems likely as the condition that leads to very high rates of reaction at low temperatures.

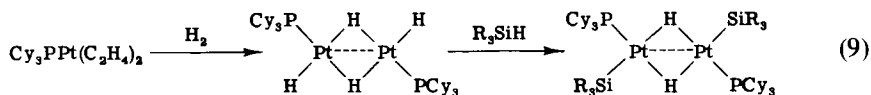
Kumada and co-workers (15) used a Pt(0) complex as a catalyst. 1-Hexene and methyldichlorosilane gave $n\text{-C}_6\text{H}_{13}\text{MeSiCl}_2$ quantitatively with bistrisphenylphosphineethyleneplatinum(0) as a catalyst.

The Pt(0) catalyst did not cause hydrosilation of internal olefins such as 2-hexene or cyclohexene, but it was effective with conjugated diolefins. With isoprene, even in excess, it produced considerable amounts of diadduct as well as 1,2-monoadduct. (This is anomalous, as will be discussed later in this review.) The principal products are shown in Eq. (8):

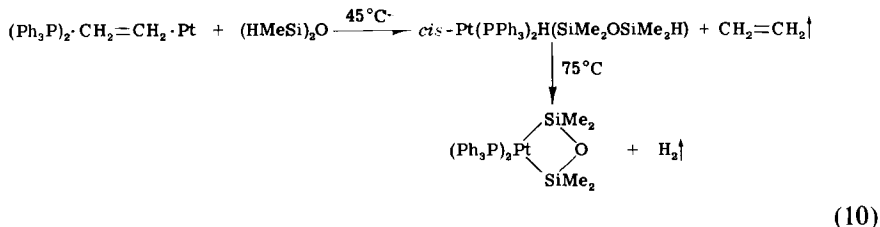


Stone and co-workers (16) recently announced that they had isolated and characterized a novel class of crystalline platinum(II) complexes prepared at room temperature by oxidative addition of hydrogen or of R_3SiH ($\text{R}_3 = \text{Me}_2\text{Et}$, $\text{Me}_2\text{CH}_2\text{Ph}$, Cl_3 , or Et_3) to $(\text{cyclo-C}_6\text{H}_{11})_3\text{P}\cdot\text{Pt}\cdot(\text{C}_2\text{H}_4)_2$. All these complexes were found to be excellent catalysts for hydrosilation

of 1-hexene, 1,5-hexadiene, styrene, 4-vinyl-1-cyclohexene, norbornene, allyl chloride, and phenylacetylene at 20°C at concentrations of 10^{-4} – 10^{-6} mole/mole of silane. The structure and yields of products looked remarkably as though chloroplatinic acid had been the source of the catalyst. However, under their mild conditions, hydrosilation of internal alkenes did not take place, nor did alkene-1 structures isomerize.



Although no exact structures of the hypothetical catalytic species have been isolated, Eaborn (17) has synthesized some compounds with many of the structural features; unfortunately, he did not examine them as catalysts for hydrosilation. A stable Pt(II) complex was isolated for study as follows:



Reikhsfel'd and his colleagues (18–18e) started with dinuclear platinum-styrene complexes, $(\text{XC}_6\text{H}_4\text{CH}=\text{CH}_2\text{PtCl}_2)_2$, as the source of the catalyst for hydrosilation of styrene. They also studied the effect of electron-donor solvents on the reaction (18c, d). Nearly identical rates of reaction were obtained when X was H, CH_3O , CH_3 , Cl, or NO_2 , with very short or no detectable induction periods at 20°C. In the absence of solvent the complexes $\text{K}[\text{Me}_2\text{SO} \cdot \text{PtCl}_3]$, $\text{cis}[\text{CH}_2=\text{CH}_2 \cdot \text{Me}_2\text{SO} \cdot \text{PtCl}_2]$, and $\text{cis}[\text{Pt}_2 \cdot \text{CH}_2=\text{CHCH}=\text{CH}_2 \cdot (\text{Me}_2\text{SO})_2\text{Cl}_4]$ gave very long induction periods and incomplete reaction. Complexes of the general form $[\text{olefin} \cdot \text{Pt}(\text{NH}_3)_2\text{Cl}]\text{NO}_3$, with ethylene, propylene, or styrene, *p*-methoxy, or *p*-chlorostyrene as the olefins caused hydrosilation of styrene to proceed very slowly and in no case to a conversion exceeding 15% at 20°C.

In the presence of electron-donor solvents or organic bases, hydrosilation of styrene did not occur. An amount of pyridine, quinoline, or triphenylphosphine equivalent to $[\text{C}_6\text{H}_5\text{CH}=\text{CHPtCl}_2]_2$ in solutions at 20°C gave a long induction period followed by hydrosilation at rates much slower than those that had been observed in absence of the bases. So-

lutions of $[\text{C}_6\text{H}_5\text{CH}=\text{CH}_2\text{PtCl}_2]_2 + 2\text{Me}_2\text{SO}$, $\text{K}[\text{Me}_2\text{SO}\cdot\text{PtCl}_3]$, $\text{CH}_2=\text{CH}_2\cdot\text{Pt}\cdot\text{Me}_2\text{SOCl}_2$, $[\text{CH}_2=\text{CHPt}_2(\text{Me}_2\text{SO})_2\text{Cl}_4]$ gave rise to the same type of kinetics but with longer induction periods and slower rates of hydrosilation. In Me_2SO no hydrosilation occurred.

These experiments show that electron-donating ligands, $\text{L}:$, which can displace olefins from π -bonded complexes with metals, prolong induction periods and sometimes completely stop hydrosilation. Most likely they form $\text{L}:\text{M}$ complexes, where $\text{L}:$ is pyridine, a phosphine, Me_2SO , or any good electron-donating ligand. If $\text{L}:$ is a substance that entirely displaces an olefin from the platinum, it is a poison preventing hydrosilation. If $\text{L}:$ displaces only some of the olefin in a reversible equilibrium, such as $\text{L}:\text{M} + \text{olefin} \rightleftharpoons \text{olefin}\cdot\text{M} + \text{L}:$, its effect is to retard hydrosilation by reducing the effective concentration of catalytic species.

Solvents, $\text{PhCH}_2\text{CH}_2\text{EtSiCl}_2$, PhMeSiCl_2 , benzene, toluene, hexane, excess styrene, or excess MeCl_2SiH , had little or no influence on the rate of hydrosilation of styrene with MeCl_2SiH . In these solvents, kinetics of hydrosilation were first-order in catalyst and zero-order for reagents, even when one of the reagents was in great excess over the other (18).

At 20°C , an induction period was observed in hexane. At 5°C an induction period of about 2 hours was seen in hexane, toluene, and styrene. This suggests that the Pt(II) complex $[\text{C}_6\text{H}_5\text{CH}=\text{CH}_2\text{PtCl}_2]_2$ became catalytic after conversion to $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2\text{PtH}(\text{—Si}\equiv)$. This conversion was not instantaneous; thus an induction period was noted, influenced by temperature and by solvents. The kinetic rate constant for formation of the phenylethylsilane was temperature dependent but nearly free of solvent effects.

To obtain reproducible kinetic data, Reiksfel'd had to add styrene to a solution of $[\text{PhCH}=\text{CH}_2\text{PtCl}_2]_2$ before MeCl_2SiH was added. When the silane was added first and styrene was withheld for about 10 minutes, the rate of hydrosilation was noticeably retarded.

This writer's explanation for these results is that reduction of $(\text{PhCH}=\text{CH}_2\cdot\text{PtCl}_2)_2$ in the absence of sufficient olefin to stabilize the product permitted Pt(0) to form. After this formed, subsequent addition of styrene did not form soluble active catalytic species. As a result, MeCl_2SiH in the absence of styrene destroyed much of the catalytic activity of the solutions in 10 minutes.

Experiments with a PtCl_6^{2-} cationic resin recently gave data very much like that from homogeneous catalysts. Reiksfel'd (18e) studied the kinetics of addition of RMe_2SiH ($\text{R} = \text{C}_6\text{H}_5$, C_6H_{11} , $p\text{-MeC}_6\text{H}_4$, and $p\text{-ClC}_6\text{H}_4$) to 1-heptene in 1/1 mole ratio with an anion-exchange resin that contained

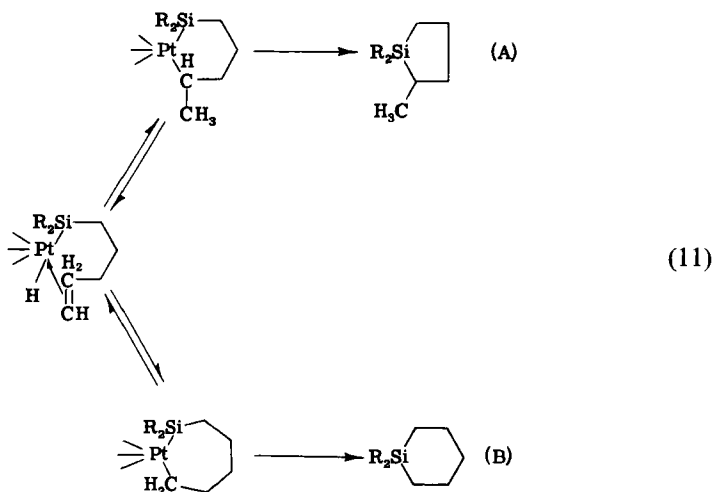
PtCl_6^{2-} as the counterion. The mixed (1/1) reagents were stirred in a thermostat at 90°C for 30 minutes before catalyst was added. Samples were removed frequently for analyses. Hydrosilation was obviously a multistage process. The last stage was first-order in catalyst and zero-order in other reagents as was found for homogeneous catalysts, but in this case the catalyst was increased in activity by adding the silane before the olefin. In the first stage the kinetics were not zero order in the other reagents.

Korolova and Reikhsfel'd (18a) also studied the kinetics of addition of RSiH_3 ($\text{R} = \text{ClC}_6\text{H}_4$, C_6H_5 , C_6H_{11} , C_4H_9 , and $i\text{-C}_5\text{H}_{11}$), to 1-hexene, 3,3-dimethyl-1-butene, and α -methylstyrene at 120° , 150° , and 180°C , and to $\text{ClC}_6\text{H}_4\text{CH}=\text{CH}_2$, $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$, and $\text{CH}_3\text{C}_6\text{H}_4\text{CH}=\text{CH}_2$ at 60° , 70° , and 80°C , usually with 5×10^{-3} mole of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in tetrahydrofuran per mole of silane. The effect of the catalyst was proportional to the amount used at 180°C . The form of the relationship was not determined, but it was felt that the catalyst was an active participant in the process. With RSiH_3 hydrosilation might proceed by a series of three consecutive steps: $\text{RSiH}_3 \xrightarrow{k_1} \text{RR}'\text{SiH}_2 \xrightarrow{k_2} \text{RR}_2'\text{SiH} \xrightarrow{k_3} \text{RR}_3'\text{Si}$. In every case $k_1 > k_2$. With $\text{C}_6\text{H}_5\text{SiH}_3$ and 1-hexene or 3,3-dimethyl-1-butene, addition proceeded through the three steps. All other examples went no further than two steps. Hydrogenation of the olefins was observed to a surprisingly large extent. α -Methylstyrene was converted to cumene to the extent of 19.5%. During the experiments, colloidal platinum was observed. The value for k_1 with $\text{C}_6\text{H}_5\text{SiH}_3$ and α -methylstyrene, at 120°C was 0.091 and at 60°C it was 0.088. For k_2 the corresponding values were 0.007 and 0.014. For this example, the rates seem either to be independent of temperature or to decrease as the temperature increased. All these data indicate that these reactions were proceeding by a mechanism very different from ones previously discussed. The products seem to be those expected from free-radical addition of RSiH_3 to olefins (19).

In recent years work has been done to combine the advantages of homogeneous catalysis with those of heterogeneous catalysts by complexing transition metals to solid inorganic or organic supports. Inorganic supports can be used if they are first treated with coupling agents, such as $(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{NMe}_2$, $(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{C}\equiv\text{N}$, $(\text{MeO})_3\text{SiCH}_2\text{CH}_2\text{C}_3\text{H}_4\text{N}$, $(\text{MeO})_3\text{Si}(\text{CH}_2)_3\text{PPh}_2$, etc. (20). Organic polymers substituted with groups that form strong bonds to transition metals may also be used (21). With Pt, Pd, or Rh complexes of this type, the solid catalysts seem to display remarkably similar results to those found with soluble catalysts with the same type ligands.

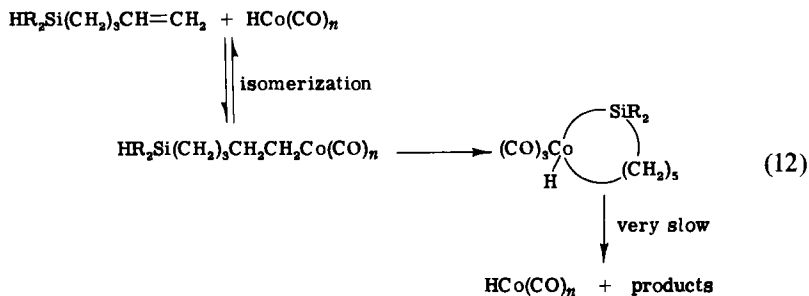
C. Ring Closure by Hydrosilation

A series of 4-pentenylsilanes was prepared of the formula, $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{SiR}_2\text{H}$ ($\text{R}_2 = \text{Ph}_2, \text{Me}_2, \text{Cl}_2, \text{PhMe}, \text{MeCl}, \text{EtCl}, \text{or } 2\text{-PrCl}$) (22). Near room temperature, chloroplatinic acid in *i*-PrOH was added to these in an amount approximately 10^{-5} mole/mole of silane. Usually a smooth reaction occurred with no external heating. Two products resulted in each example which are thought to form by an intermediate complex as follows:



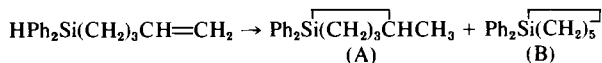
Silacyclopentanes (A) were the principal products in every case. The A/B ratio varied with R from a high of 22 when $\text{R}_2 = \text{Ph}_2$ to a low of 4 when $\text{R}_2 = \text{Cl}_2$ (see Table I).

Steps in the mechanism with cobalt are believed to be as follows:



Swisher and Chen (23) studied the effect of varying n in

TABLE I

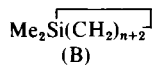
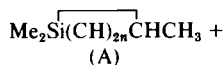


Catalyst	% Yield	Solvent	Temperature (°C)	A/B
$\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$	93.3	Neat	20	20-22
Ph-alanine · Pt · $\text{C}_2\text{H}_4 \cdot \text{Cl}_2$	89.3	Toluene	80	Only A
L-Proline · Pt · <i>trans</i> - $\text{C}_4\text{H}_8 \cdot \text{Cl}$	89.3	Toluene	80	Same
L-Proline · Pt · <i>cis</i> - $\text{C}_4\text{H}_8 \cdot \text{Cl}$	78.2	Toluene	80	Same
$(\text{Ph}_3\text{P})_4\text{RhCl}$	89.0	Neat	80	6.6
$[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2^a$	98.1	Hexane	80	16
	23.9	Hexane	80	7.9
$\pi\text{-C}_5\text{H}_5\text{Co}(\text{CO})_2^a$	36.9	Neat	135	4.2
$\text{Co}_2(\text{CO})_8$	Nil			

^a $\text{HPhMeSi}(\text{CH}_2)_3\text{CH}=\text{CH}_2$.

$\text{HMe}_2\text{Si}(\text{CH}_2)_n\text{CH}=\text{CH}_2$ between 0 and 6 on the products made with chloroplatinic acid in dilute solution in hexane at reflux for 48 hours. With $n = 0$ or 1, no cyclic products could be detected but polymers formed of the formula $[-\text{Me}_2\text{Si}(\text{CH}_2)_{2+n}-]_x$. The effect of n was dramatic on the rate of reaction and the yield of products, as summarized in Table II.

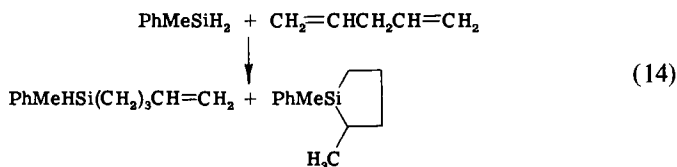
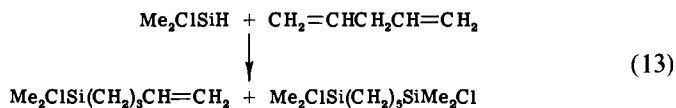
Fessenden and Kray (24) showed that 5-dimethylsilyl-1-hexene with chloroplatinic acid in pentane gave a 73% yield of *cis*- and *trans*-1,1,2,5-tetramethylsilacyclopentane.

TABLE II
 $\text{HMe}_2\text{Si}(\text{CH}_2)_n\text{CH}=\text{CH}_2 \rightarrow$ 

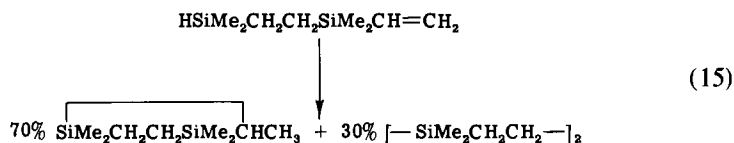
n	% Yield	A/B
2	46.3	0/100
3	58.1	90/10
4	69.8	52.5/47.5
5	16.4	54.2/45.8
6	2.4	100/0

Kobrakov *et al.* (25) studied addition of R_2SiH_2 ($R_2 = ClCH_2$, Me; Et, Cl; and Ph, Me) to 1,4-pentadiene with chloroplatinic acid. They obtained yields of the silacyclopentanes and silacyclohexanes of only about 20%, the remainder going to polymers, although the reaction proceeded smoothly. The poor yield of cyclics is probably due to the fact that hydrosilation took place in steps, the first step giving $HR_2Si(CH_2)_3CH=CH_2$. Compounds of this type give excellent yields of cyclics when they react alone, but in these experiments this intermediate was formed under conditions of a competitive reaction. It could cyclize or add a second mole of R_2SiH_2 to form $HR_2Si(CH_2)_5SiHR_2$. This then could add to 1,4-pentadiene or to the intermediate to form oligomers.

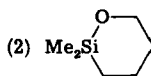
The addition of $ClCH_2MeSiH_2$, $EtClSiH_2$, and $PhMeSiH_2$ as well as Me_2ClSiH to 1,4-pentadiene was studied with chloroplatinic acid (25).

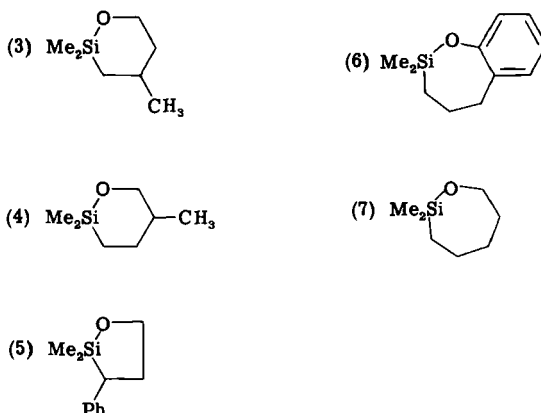


The following cyclization took place readily to favor formation of a disilacyclopentane:



Mironov *et al.* (26) showed that a variety of alkenoxysilanes form cyclic hydrosilation products readily with chloroplatinic acid. Good yields of cyclic products were found, of which the following are examples:





The structures obtained from $\text{HSiMe}_2(\text{CH}_2)_n\text{CH}=\text{CH}_2$ by Swisher (23) suggest that the structures assigned to **2**, **4**, **6**, and **7** may not be correct, unless oxygen in the chain had a very different effect than $-\text{CH}_2-$ on ring closures. Alkynyloxysilanes such as $\text{HMe}_2\text{SiOCH}_2\text{C}\equiv\text{CH}$ only formed polymeric structures.

Mironov *et al.* (26) also tried to cyclize acyloxysilanes with some success in making a series of silalactones. They used the series $\text{HMe}_2\text{SiOOC}(\text{CH}_2)_n\text{CH}=\text{CH}_2$ ($n = 0, 1, 2, 8$). When $n = 0$, vinylpolymerization of the acrylate occurred. This was also true for crotonic, cinnamic, and methacrylic esters to complicate and confuse the experiments, but with $n = 1, 2$, or 8 , the compounds reacted readily.

The structures of the products were thought to be $\text{Me}_2\text{SiOOC}(\text{CH}_2)_{n+2}$, but they might have been $\text{Me}_2\text{SiOOC}(\text{CH}_2)_n\text{CHCH}_3$. When $n = 8$ the product might have been a polymer. A cyclic was isolated by distillation under high vacuum and high temperature which would likely depolymerize a polymer to give a volatile cyclic. All these lactones were noticeably unstable, with molecular weights varying with time as they dimerized, trimerized, etc.

D. Side Reactions of Catalytic Species

Experiments with trichlorosilane-d, Cl_3SiD , were most instructive about side reactions that can take place in the hypothetical catalytic olefin $\cdot\text{PtH}(-\text{Si}\equiv)$ species during hydrosilation. Although trichlorosilane-d and methyldichlorosilane showed no exchange of deuterium and hydrogen at 100°C during many hours in the absence of a catalyst, traces

of chloroplatinic acid caused very rapid exchange at room temperature (27). Thus, Eq. (7) was a reversible process.



Sommer showed in an elegant study with optically active α -naphthylphenylmethylsilane, $\text{R}_3\text{Si}^*\text{H}$ (28), that an exchange of this kind can be faster than hydrosilation.

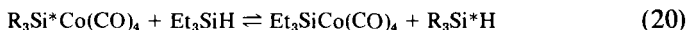
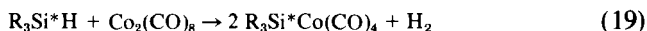


Chloroplatinic acid, as well as $[(\text{C}_2\text{H}_4)\text{PtCl}_2]_2$, $\text{IrClCO}(\text{PPh}_3)_2$, $\text{Co}_2(\text{CO})_8$, $\text{R}_3\text{Si}^*\text{Co}(\text{CO})_4$, 10% Pd/C, 5% Pt/C, and Raney Ni were effective catalysts for reaction (17).

Dicobalt octacarbonyl and bis(triphenylphosphine)carbonyl chloroiridium catalyzed analogous hydrogen-deuterium exchanges (28).



An intermediate was isolated, and underwent an exchange:



A comparable exchange occurred between (–)-phenylneopentylmethylsilylcobalt tetracarbonyl and triphenylsilane. All these exchanges proceeded with retention of configuration of the asymmetric center of the silane.

Studies of hydrosilation with trichlorosilane-d (2f) proved that exchange can also take place between SiD and C—H bonds in olefins during hydrosilation. Isobutylene was chosen as the olefin for this study because both it and isobutyltrichlorosilane have ^1H NMR spectra that are easy to interpret, and because movement of the double bond can give rise to no detectable isomerization. Excess trichlorosilane-d with isobutylene and chloroplatinic acid was sealed into a Pyrex tube and kept near 25°C overnight. Deuterosilation was complete in less than 1 hour. Analysis of the product after about 16 hours indicated reactions that can be summed up as follows:



The tertiary position of the isobutylsilane was only about 70% deuterated, and deuterium was on every carbon atom in the system, so the i-butyltrichlorosilane contained an average of 2.5 D's and 6.5 H's per mole. This gives a D/H ratio in the i-butyl group of 0.39. If D's and H's

in the original solution became randomly distributed among every possible structure, the ratio would be $D/H \approx 0.44$.

A random distribution of D's and H's was almost achieved in this example. Such a result required many exchange steps before hydrosilation; i.e., these exchanges were much faster than the formation of the alkylsilane. The alkylsilane left the complex as the last, irreversible, relatively slow step in hydrosilation.

Isobutylene recovered from an experiment with a mole ratio of 3 olefins/ Cl_3SiD contained C—D bonds. This requires that deuterioisobutylene was displaced by isobutylene from the complex in a reversible way to lead to equilibrium between olefin molecules in solution and those in the complex.

$Cl_3Si-i-C_4H_6.5D_{2.5}$ was employed as a solvent during the addition of Cl_3SiH to 1-octene with chloroplatinic acid. Excess Cl_3SiH was recovered free of Cl_3SiD , and this indicates that the solvent in no way participated in the several equilibria. Similar experiments with Cl_3Si-D and other olefins are summarized in Table III.

Harrod and Chalk (11*d*) extended this type of study by examining the effects of rhodium and palladium complexes on isomerization of olefins substituted with deuterium at specific points in the molecule. They used 1-pentene-1,2- d_2 , $CH_3CH_2CH_2DC=CHD$, and 1-heptene-3- d_2 , $C_4H_9CD_2CH=CH_2$. Rhodium was used near room temperature at a concentration of about $10^{-3} M$ $RhCl_3 \cdot 3H_2O$ and palladium as 10^{-2} – $10^{-3} M$ $(PhCN)_2PdCl_2$ at $55^\circ C$. They studied the distribution of deuterium in the deuterated olefins and also the distribution of deuterium in mixtures of 1-heptene-3- d_2 and 1-pentene as a function of time during isomerization. The two catalysts displayed different effects. Rhodium trichloride seemed to resemble chloroplatinic acid in causing rapid redistribution of deuterium onto all the carbon atoms in the system, indicating rapid reversible addition of hydride to coordinated olefin. With palladium, double-bond shifts seemed to occur by a 1,3 shift of a deuterium or hydrogen, with much less intermolecular exchange. Very little deuterium became attached to doubly bonded carbon atoms. With deuteriopentene, 1,3 shifts only like those in Eq. (22) seem to best fit the results.

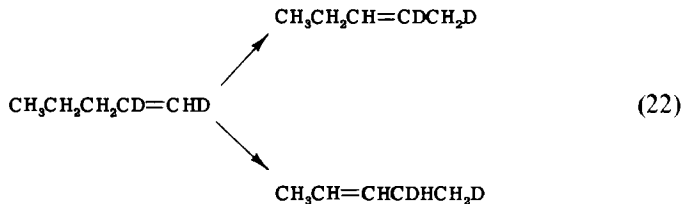
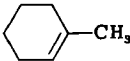

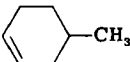


TABLE III
EXCHANGE OF SiD AND C—H DURING HYDROSILATION WITH Cl_3SiD^a

Olefin	D/H Mixture	D/H Adduct	Structure of products
$\text{CH}_2=\text{CH}(\text{CH}_3)_2$	0.44	0.39	$\text{Cl}_3\text{SiC}-\text{C}-(\text{C})_2$
$\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CH}_3$	0.28	0.25	$\text{Cl}_3\text{Si}-n-\text{C}_8$
$\text{CH}_2=\text{CHCH}(\text{CH}_3)_2$	0.26	0.20	(A) 90% $\text{Cl}_3\text{SiC}-\text{C}-\text{C}-(\text{C})_2$ <div style="text-align: center;"> $\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C} \end{array}$ </div>
$(\text{CH}_3)_2\text{C}=\text{CHCH}_3$	0.22	0.20	(B) 10% $\text{Cl}_3\text{SiC}-\text{C}-\text{C}-\text{C}$ 70% (A); 30% (B)
	0.37	0.28	Mostly $\text{Cl}_3\text{SiC}-$ 
	0.30	0.31	Same
Cyclo- C_6H_{10}	0.29	0.23	$\text{Cl}_3\text{Si}-\text{cyclo-C}_6$
$\text{CH}_3\text{PhC}=\text{CH}_2$	0.24	0.1	$\text{Cl}_3\text{SiCH}_2\text{CDPhCH}_3$
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}-\text{CH}_2\text{Cl} \\ \\ \text{CH}_2=\text{CHCH}_2\text{Cl} \end{array}$	0.84	0.14	95% $\text{Cl}_3\text{SiCH}_2\text{CD}(\text{CH}_3)\text{CH}_2\text{Cl}$
$\text{CH}_2=\text{C}-\text{CH}_2\text{Cl}$ $\text{CH}_2=\text{CHCH}_2\text{Cl}$	Excess $\text{C}_3\text{H}_5\text{Cl}$		$\text{Cl}_3\text{SiCH}_2\text{CHDCH}_2\text{Cl} +$ $\text{CH}_2=\text{CHCH}_2\text{D}$
$\text{PhC}\equiv\text{CPh}$	0.45	0.1	$\begin{array}{c} \text{Ph} \quad \text{Ph} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{D} \quad \text{SiCl}_3 \end{array}$

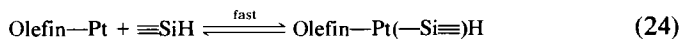
^a From Benkeser and Cunico (29)

These data may be rationalized as the results of processes occurring in the coordination sphere of a transition metal not necessarily in the following order:

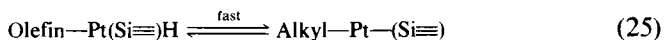
(a) Olefin¹-olefin² exchange:



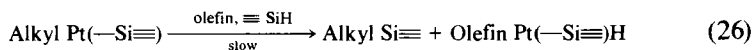
(b) Reversible oxidative addition:



(c) Isomerization of olefin:

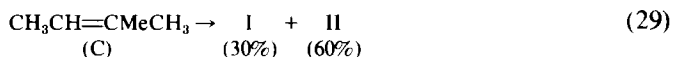
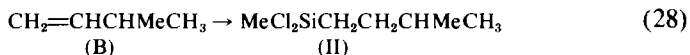
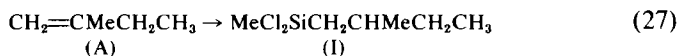


(d) Hydrosilation:



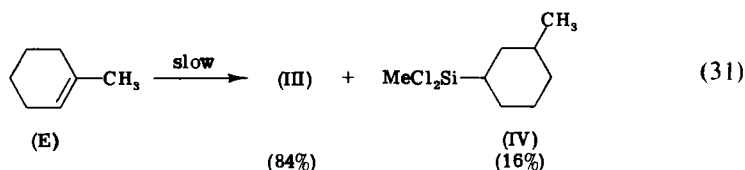
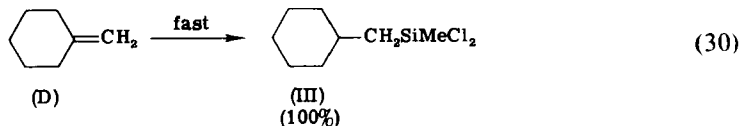
Rates of reaction and the course of each step depended upon the structures of the species. With α -methylstyrene and with methallyl chloride, steps (b) and (c) were not detectable; perhaps (a) did not happen and the product was that of direct addition with no exchanges or isomerization. With 1-hexene, 3-methyl-1-butene-1, 3-methyl-2-butene, and cyclohexene the exchanges and isomerization were much faster than step (d). By step (d) the product left the coordination sphere of the metal and no longer participated in any of the processes.

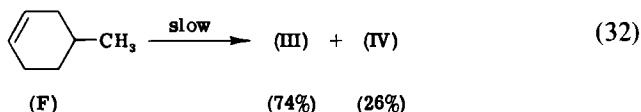
Excess MeCl_2SiH with each of the methylbutenes (2f) formed the following products:



Excess MeCl_2SiH added slowly to **A** at reflux gave 82% of compound **I** and 18% of **II**. One equivalent of MeCl_2SiH was added to solutions of one equivalent of both **A** and **B** or **A** and **C**. In either case the recovered olefin was largely **C**. The relative yields of **I** and **II** from the competitive reactions would indicate relative reactivities of **B/A/C** of 1/0.07/0.02. **B** was apparently more reactive than **A** or **C**. This suggests that **C** formed from **B** and **A** after most of the **II** or **I** was made. If **A** and **B** formed **C** before hydrosilation, the three olefins should exhibit relative reactivities close to 1/1/1, and they should each have made the same mixture of adducts.

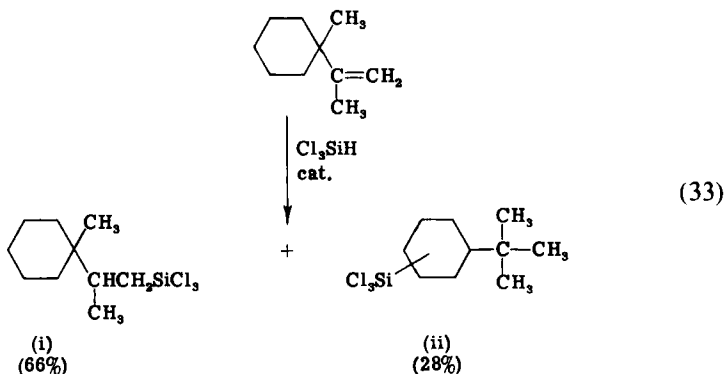
Similar experiments were carried out with the following olefins in excess:





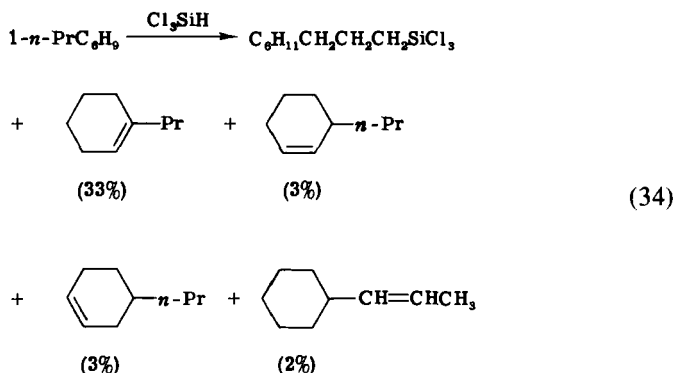
In each case excess olefin was recovered as **E** and **F**: 87% **E** in (30), 93% **E** in (31), and 74% **E** in (32). Hydrosilation of **D** was very rapid to make pure **III**. Hydrosilation of **E** and **F** was incomplete after 48 hours at reflux.

Benkeser and Cunico (29) found that Cl_3SiH at 140°C with either 1- or 4-*tert*-butylcyclohexene and dichlorobis(ethylene)- μ,μ -dichlorodiplatinum(II) gave rise to skeletal rearrangement of the olefins and made (i) 1-trichlorosilyl-2-(1-methylcyclohexyl)propane and (ii) *tert*-butyltrichlorosilylcyclohexane very slowly. The formation of (i) required a 1,2 migration of a methyl group from the *tert*-butyl group. Even more unusual was the finding that this migration was reversible, as demonstrated by the fact that 1-methyl-1-isopropenylcyclohexane also made (i) and (ii) together with a small amount of *tert*-butylcyclohexane. Olefins recovered from all these experiments were mixtures of *tert*-butylcyclohexenes approximately at thermodynamic equilibrium.



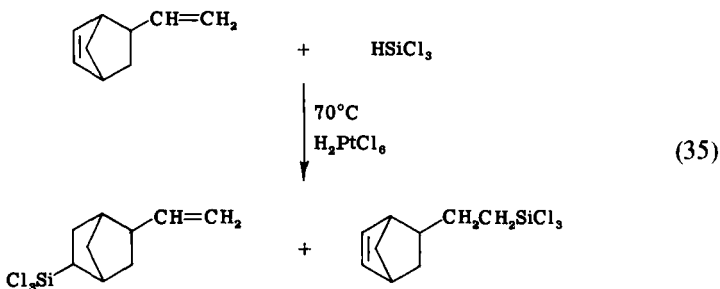
In continuing the study of hydrosilation of alkylcyclohexenes, Benkeser *et al.* (13) studied in detail the addition of Cl_3SiH (with H_2PtCl_6) to 1-, 3-, and 4-ethylcyclohexenes, as well as to ethylidene- and vinylcyclohexenes. With an olefin/ Cl_3SiH ratio of 1/1.9 at reflux, vinylcyclohexane gave a 68% yield of adduct in 0.5 hours. The other olefins required much more time: e.g., 96 hours was needed to achieve 83% yield from 3-ethylcyclohexene. Each olefin made the same adduct— $\text{C}_6\text{H}_{11}\text{CH}_2\text{CH}_2\text{SiCl}_3$ —and recovered olefins were mixtures of all possible

isomers except vinylcyclohexane. They studied 1-Pr-cyclohexene with the following results:



Hydrosilation of alkylcyclohexenes illustrates the ability of active catalytic complexes to isomerize olefins and the tendency chlorosilanes have to form primary alkyl adducts even if this requires a skeletal rearrangement of the olefin. Addition to $\text{CH}_2=\text{C}$ groups can be rapid at low temperatures. Addition to internal olefins is slower, but still fast if a terminal position is conveniently available. Addition to cyclohexene structures is very slow and accompanied by every conceivable exchange and isomerization.

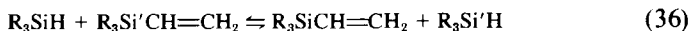
Every example with a cyclohexene has proved hydrosilation to be very slow and difficult, but this difficulty was not experienced with cyclopentene structures by Petrov *et al.* (27). A number of chlorosilanes were added to bicyclo-(2,2,1)-hept-5-ene, bicyclo-(2,2,1)-hepta-2,5-diene, 2-methyl- and 2-vinylbicyclo-(2,2,1)-hept-5-ene, and dicyclopentadiene under mild conditions. Particularly surprising was the example of Eq.



(35), in which a vinyl group and a cyclopentene apparently reacted at similar rates.

Unpublished work from our laboratory (*12b*) indicated that triethoxysilane behaved differently than trichlorosilane. With linear olefins and chloroplatinic acid in a ratio of $1:5 \times 10^{-3}$ it added much more slowly, did not isomerize the olefin, and formed secondary alkyltriethoxysilanes. However, it added rapidly to allyl acetate (see Table IV).

A series of silanes, Me_2ClSiH , MeCl_2SiH , Cl_3SiH , and Me_2PhSiH were added to vinylsilanes, $\text{Me}_3\text{SiCH}=\text{CH}_2$, $\text{Me}_2\text{ClSiCH}=\text{CH}_2$, $\text{MeCl}_2\text{SiCH}=\text{CH}_2$, and $\text{Cl}_3\text{SiCH}=\text{CH}_2$, with 10^{-4} moles of chloroplatinic acid per mole of vinylsilane at 100°C (*12a*). These reactions were characteristically fast and went to completion smoothly, but they always yielded at least two products and sometimes four. All combinations of reagents gave $\text{R}_3\text{SiR}_3\text{Si}'\text{CHCH}_3$ as well as the principal product $\text{R}_3\text{SiCH}_2\text{CH}_2\text{Si}'\text{R}_3$. When R_3Si and $\text{R}_3\text{Si}'$ were different two more products appeared, which proved to be $\text{R}_3\text{SiCH}_2\text{CH}_2\text{SiR}_3$ and $\text{R}_3\text{Si}'\text{CH}_2\text{CH}_2\text{Si}'\text{R}_3$. These are explained as products resulting from a vinyl-H exchange:



The products are easily identified when one of the silyl groups is PhMe_2Si . Table V illustrates the products that form in this case.

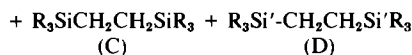
No unusual products were formed with allylsilanes. Under similar conditions, allylsilanes made only 1,3-disubstituted propanes, and propenylsilanes were recovered if excess allylsilane was used.

TABLE IV
 $(\text{EtO})_3\text{SiH} + \text{OLEFINS} \xrightarrow{100^\circ\text{C}} \text{PRODUCTS}$

Olefin	Silane/olefin	Days	% Conv.	Products
1-Hexene	1/1	10	83	$(\text{EtO})_3\text{Si}-n\text{-C}_6\text{H}_{13}$
2-Hexene	1/2	1 (150°)	24	1,2,3- $\text{C}_6\text{H}_{13}\text{Si}(\text{OEt})_3$ ratio: 14.5/1/0.9
3-Hexene	1/1	1	~Nil	1- and 3- $\text{C}_6\text{H}_{13}\text{Si}(\text{OEt})_3$
		24	36	Ratio: 1/2.1
Allyl acetate	2/1	1 ^a	100	$(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{OAc}$ (82%) + $(\text{EtO})_3\text{SiOAc}$ (18%)

^a This solution reacted rapidly even at room temperature.

TABLE V



GLC Area (%)					
R_3Si	R_3Si'	A	B	C	D
PhMe ₂ Si	Cl ₃ Si	88.3	8.9	1.6	1.3
PhMe ₂ Si	MeCl ₂ Si	90.6	7.8	0.7	0.9
PhMe ₂ Si	Me ₂ ClSi	94.7	3.7	0.8	0.8
Cl ₃ Si	PhMe ₂ Si	76.5	19.8	2.1	1.6
MeCl ₂ Si	PhMe ₂ Si	75.8	17.0	4.1	3.1
Me ₂ ClSi	PhMe ₂ Si	86.6	2.6	5.5	5.3

E. Asymmetric Hydrosilation with Chiral Platinum Complexes

The recent discovery that a chiral phosphine ligand in a platinum(II) complex can give rise to a catalytic asymmetric hydrosilation of prochiral olefins seems to prove that a phosphine ligand can be included in the coordination sphere of platinum in an active catalytic species, but that when a phosphine ligand is so included, the activity of the species is reduced by several orders of magnitude.

Kumada *et al* (30) achieved for the first time a catalytic asymmetric hydrosilation with a platinum complex by addition of silanes to prochiral olefins. *cis*-Dichloro(ethylene)-*S*-1-phenylethylamine platinum(II) was a very efficient catalyst, but the adducts were always racemic. However, *cis*-dichloro(ethylene)phosphine platinum(II) with chiral phosphine ligands gave rise to optically active adducts (31). The procedure to evaluate the catalysts was typically as follows: A solution of an olefin (30 mmoles), a chlorosilane (30 mmoles), and a catalyst (0.02 mmoles) was heated to 40°C in a sealed glass tube for 24 hours, and then analyzed. Under these conditions, complexes *cis*-L*₂PtCl₂ were not effective as catalysts. Catalysts [L*PtCl₂]₂ and *cis*-C₂H₄L*PtCl₂ were effective catalysts. [L* was L*¹ = (R)PhCH₂MePhP; L*² = (R)MePh-*n*-PrP; and L*³ = (-)-menthyl-Ph₂P]. Asymmetry in these ligands centered on phosphorus in the first two ligands but on the menthyl group in the third.

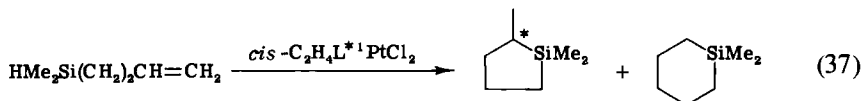
The extent of asymmetric induction was low. L*¹ was the most effective to induce asymmetry in the adduct of α -methylstyrene and methyl-

dichlorosilane. A consistent preference for formation of the (*R*) isomer of the adducts suggested that a similar stereochemical sequence of coordination of olefin to platinum followed by addition of silane occurred, i.e., that a similar disastereomeric transition state was involved in every case.

Methyldichlorosilane was by far the most reactive in hydrosilation of 1,1-disubstituted olefins. Trialkylsilanes did not add at all, even at 120°C. Trichlorosilane gave complicated results involving isomerization of olefins and dimerization of α -methylstyrene, and products were not optically active. 2-Methylbutene-2 and trichlorosilane gave two adducts, 2-methylbutyltrichlorosilane and 3-methylbutyltrichlorosilane. The latter required isomerization of the olefin. 2,3-Dimethylbutene-1 gave one adduct in 70% yield, and it was optically slightly active [0.8% (*R*) isomer].

Asymmetric hydrosilation of prochiral olefins other than 1,1-disubstituted ones was unsuccessful because they were unreactive under the conditions employed. Styrene afforded a 20% yield of 1-phenylethyl- and 50% of 2-phenylethylmethyldichlorosilane, both inactive. The 1-phenylethyl isomer had a possibility of activity with its asymmetric center, $\text{PhMeC}^*\text{HSi}\equiv$.

A most interesting example of an asymmetric ring closure was observed:



Kumada *et al.* (32) had shown earlier that these same catalysts add methyldichlorosilane to alkylphenyl ketones to give optically active alkylphenyl carbinols.



III

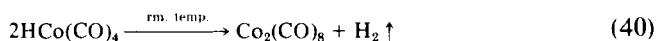
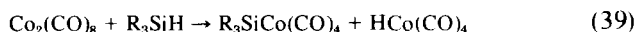
HOMOGENEOUS CATALYSIS WITH METALS OTHER THAN PLATINUM

Dicobaltoctacarbonyl at concentrations about $10^{-3} M$ was an excellent catalyst (*11b*) for hydrosilation of 1-hexene by common silanes, including $(\text{MeO})_3\text{SiH}$, Et_3SiH , and PhCl_2SiH , to give exclusively *n*-hexyl silanes. The only observable side reaction was formation of hexene-2 and hexene-

3. Isomerization was faster than hydrosilation and more facile than with platinum or rhodium catalysts. Isomerization occurred with $(\text{MeO})_3\text{SiH}$, which does not cause isomerization with platinum. These hydrosilations were most successful below 60°C and proceeded smoothly even at 0°C after an induction period. Above 60°C , the catalyst decomposed and became ineffective.

If the catalyst was added to the silane and allowed to react with it prior to the addition of the hexene-1, catalytic activity was largely or completely lost. Also, the rate of hydrosilation and isomerization was markedly reduced when the concentration of silane exceeded that of 1-hexene.

The mechanism suggested to explain these results is as follows:



The silylcobalt compound of reaction (39) is thought to be neither catalytic nor capable of adding to an olefin in a manner analogous to reaction (41). Kumada (32) described catalytic activity for several nickel(II) complexes for hydrosilation of 1-alkenes with methylchlorosilane at 120°C for 20 hours in a mole ratio of olefin/silane/catalyst of $1/2/10^{-3}$. $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$, $\text{Ni}(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)\text{Cl}_2$, and $\text{Ni}(\text{dipyridine})\text{Cl}_2$ were practically ineffective. However, $\text{Ni}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)\text{Cl}_2$, $\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Cl}_2$, and dichloro[1,1'-bis(dimethylphosphino)ferrocene]nickel(II) were effective not only for hydrosilation but for H-Cl exchange, so that the principal products were $\text{RMeSiClH} + \text{MeSiCl}_3$. With 1-octene and the last catalyst named above, $\text{C}_8\text{H}_{17}\text{MeSiClH}$ and $\text{C}_8\text{H}_{17}\text{MeSiCl}_2$ were obtained in the ratio of 87/18.

Kumada and his co-workers (33) later showed that a chiral Ni(II) complex induced asymmetric hydrosilation of α -methylstyrene by methylchlorosilane at 90°C for 60 hours. By use of the *trans*-(*R*) isomer of $(\text{PhCH}_2\text{—PhMeP}^*)_2\text{NiCl}_2$, they isolated 8% $\text{PhMeC}^*\text{HCH}_2\text{SiMeClH}$ with $[\alpha]_D + 6.43^\circ$ and 31% $\text{PhMeC}^*\text{HCH}_2\text{SiMeCl}_2$ with $[\alpha]_D + 6.50^\circ$. The latter compound was treated with methyllithium to prepare $\text{PhMeC}^*\text{HCH}_2\text{SiMe}_3$, $[\alpha]_D + 10^\circ$, which they estimated as 17.6% optically pure.

The square-planar complex (34) $\text{NiCl}_2 \cdot (\text{P-}i\text{-Bu}_3)_2$ was a better catalyst than the tetrahedral complex $\text{NiBr}_2 \cdot (\text{PPh}_3)_2$ for hydrosilation of styrene with trichlorosilane at temperatures of $150^\circ\text{--}170^\circ\text{C}$. A nickel(0) complex, $\text{Ni}[\text{P}(\text{OPh})_3]_4$, was as good as $\text{NiCl}_2(\text{NC}_5\text{H}_5)_4$, which was best among known nickel catalysts for this reaction. Addition of copper(I) chloride

increased the yield from about 10% to about 75% of product and made it almost exclusively 1-phenyl-1-trichlorosilylthane (35). These catalysts were used at about 0.2 wt% in 1/1 styrene/trichlorosilane, usually at 150°C for more than 3 hours.

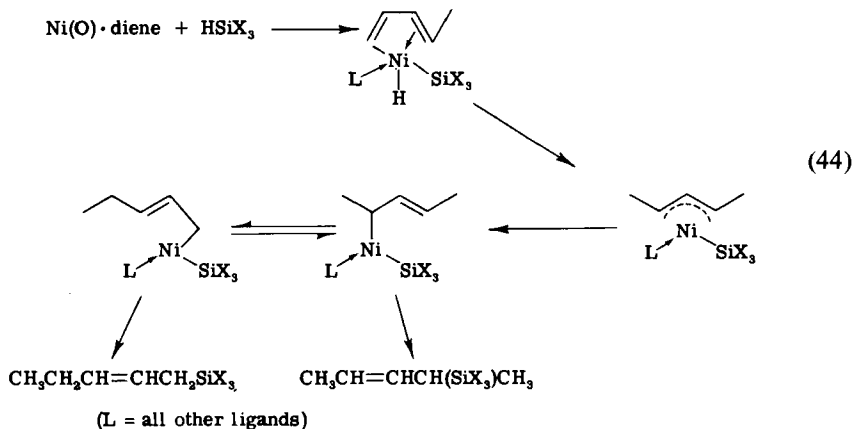
The activity of Ziegler-type systems such as $M(\text{acac})_n\text{-AlEt}_3$ ($M = \text{Cr, Mn, Fe, Co, or Ni}$; $\text{acac} = \text{acetylacetonate}$) was examined with 1-olefins and triethyl- or triethoxysilanes (35). Systems with nickel or cobalt showed low activity for hydrosilation but isomerized the olefin and were reduced to the metal. The study was extended to dienes and acetylenes (36). Isoprene gave the same products with these catalysts as are made with chloroplatinic acid. Penta-1,3-diene with Pt gave 1-methylbut-2-enylsilanes. The Ziegler catalysts gave mainly penta-2-enylsilanes



where $X = \text{OEt, Et, Cl}_2\text{Me, Me}$. Only when $X = \text{OEt}$ was some 1-methylbut-2-enylsilanes also formed.

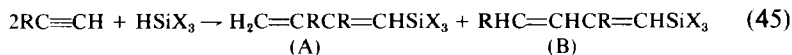
With dienes and acetylenes, only $M = \text{Fe, Co or Ni}$ showed activity. The Fe and Co systems gave many side products. Therefore, the Ni catalyst was studied in greater detail. Bis-(π -cycloocta-1,5-diene)nickel(0) was equivalent to the Ziegler catalyst in hydrosilation of penta-1,3-diene.

A mechanism suggested for this system is essentially identical to that already discussed, but adapted to a diene.

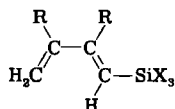


These Ziegler catalysts were inactive for hydrosilation of cyclopentadiene, *cis,cis*-cycloocta-1,5-diene, or norbornadiene.

With Ziegler systems containing Ni, terminal acetylenes gave coupled diadducts as in Eq. (45):



where $\text{R} = n\text{-C}_3\text{H}_7$ and $\text{X} = \text{OEt}$. At 0°C the system of Eq. (45) was exothermic and gave 80% A and 20% B. Two geometric isomers of A are possible, but only



was detected. The system was active with other alkylacetylenes but inactive with all internal acetylenes.

The relative rate constants for addition of $\text{XC}_6\text{H}_4\text{Me}_2\text{SiH}$ to ethylene were measured with H_2PtCl_6 , $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$, and $\text{Co}_2(\text{CO})_8$ as catalysts (37). The relative amounts of these three catalysts that gave approximately equal rates of addition were 1 Pt = 20 Rh = 4000 Co. The additions seemed to be first-order with respect to ethylene, which may be an artifact resulting from the rate of solution of the gaseous ethylene in the liquid medium of the reaction. In each case the relative rate of hydrosilation was nearly independent of the structure of X. The relative rate constants of $\text{Et}_{3-n}\text{Cl}_n\text{SiH}$ to 1-heptene and $n\text{-Pr}_{3-n}(\text{EtO})_n\text{SiH}$ to 1-hexene with H_2PtCl_6 were studied (37) in sealed ampoules at 120°C for 4 hours with tenfold excesses of olefin. The calculated relative rates for $\text{Et}_3\text{SiH}/\text{Et}_2\text{ClSiH}/\text{EtCl}_2\text{SiH}/\text{Cl}_3\text{SiH}$ were 1/1.94/2.64/3.0; for $n\text{-Pr}_3\text{SiH}/n\text{-Pr}_2\text{EtOSiH}/n\text{-Pr}(\text{EtO})_2\text{SiH}/(\text{EtO})_3\text{SiH}$ they were 1/4.33/15.26/11.25.

Unpublished work in this laboratory convinced us that the method of competing two reagents for an excess of a third usually does not offer a reliable measure of relative reactivities for either olefins or $\equiv\text{SiH}$ compounds in hydrosilation with platinum catalysts. To obtain valid relative rate data, each competing species must react as though the other were not present. This situation does not obtain during hydrosilation. When the catalytic species has $\equiv\text{SiH}$ and olefin molecules exchanging rapidly in the coordination sphere of the metal accompanied by isomerization of the olefin, exchange of C—H and Si—H bonds, etc., two kinds of $\equiv\text{SiH}$ molecules or two kinds of olefins permit so large a number of rapidly changing transition states that the rate of formation of products becomes unpredictable. Our data agree with that of Reiksfel'd in that at low temperatures in reactive systems the reaction is first-order in catalyst and zero-order with respect to reagents. Ratios of rate constants that were measured absolutely were seldom close to what should have been

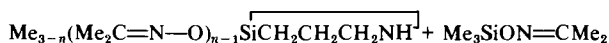
the same ratio as measured by the method of competitive reactions. The methods agreed best when the ratio $k_1/k_2 \approx 1$. When the ratio was not close to unity, the method of competitive reactions made that reagent with a smaller absolute rate constant win in competition with reagents with larger rate constants. This anomaly can be plausibly explained as follows: That reagent which makes the more stable Olefin-MH($-\text{Si}\equiv$) complex has the slower overall absolute rate of hydrosilation, but by monopolizing the catalyst, it tends to exclude very reactive reagents during competitive reactions.

The method of competitive reactions was used (38) to measure the relative rates of addition of $\text{Et}_{3-n}\text{Cl}_n\text{SiH}$ ($n = 0-3$) to 1-heptene with $\text{Co}_2(\text{CO})_8$ and $\text{RhCl}(\text{PPh}_3)_3$ as catalysts. With the rhodium catalyst at 80°C no hydrosilation took place; at 120°C only that silane with a greater number of Si-Cl bonds yielded products.

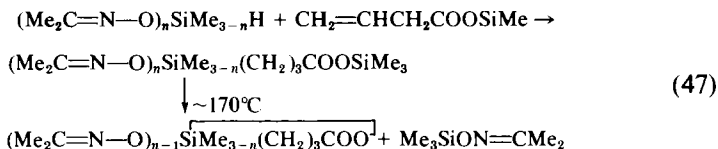
These experiments seem to show that the relative reactivities of $\text{Et}_3\text{SiH} : \text{Et}_2\text{ClSiH} : \text{EtCl}_2\text{SiH} : \text{Cl}_3\text{SiH}$ were approximately $1 : 2 \times 10^2 : 4 \times 10^4 : 8 \times 10^6$. The relative rates are made obviously misleading by the fact that Et_3SiH in the absence of a chlorosilane reacted smoothly with 1-heptene at 60°C . To obtain a measurable amount of products with $\text{Co}_2(\text{CO})_8$, about 100 times more catalyst had to be used. In this case, the relative rates were calculated to be Cl_3SiH (1); EtCl_2SiH (1.3); Et_2ClSiH (1.5); Et_3SiH (1.6). Similar experiments with ethoxysilanes at 80°C with the same catalysts gave the following calculated relative rate constants: with Rh, $(n\text{-Pr})_3\text{SiH}$ (1); $(n\text{-Pr})_2\text{EtOSiH}$ (5.4); $n\text{-Pr}(\text{EtO})_2\text{SiH}$ (28.4); $(\text{EtO})_3\text{SiH}$ (42.8); with $\text{Co}_2(\text{CO})_8$, the values were 1; 27.5; 59.5; 11.9.

Catalysts of the type $\text{L}_2\text{RhH}(\text{SiR}_3)\text{Cl}$ were studied (39). These catalysts were used to add Et_3SiH to 1-hexene in benzene in a mole ratio of $10^{-4} : 1 : 2 : 4.5$ at 50°C . An induction period seems to have been present. After about 20 minutes, hydrosilation took place with a several degree rise in the temperature of the solution. The excess hexene was isomerized to 2- and 3-hexenes, mostly trans isomers. The order of increasing catalytic efficiency for L_3RhCl was $\text{L} = (\text{cyclo-C}_6\text{H}_{11})_3\text{P} \ll \text{Ph}_2\text{MeP} < \text{Ph}(\text{cyclo-C}_6\text{H}_{11})_2\text{P} \approx \text{Ph}_3\text{P} < \text{Ph}_2\text{-cyclo-C}_6\text{H}_{11}\text{P} \approx \text{Ph}_2\text{EtP}$.

Successful hydrosilations were carried out with chloroplatinic acid and the uncommon reagents shown in the following equations with $n = 2$ and 3 (40):



The heterocyclic aminosilane tended to dimerize and trimerize on storage.



Rejhon and Hetflejs (40) recently investigated the hydrosilation of 1-hexene with triethyl, triethoxy, and trichlorosilane, and found that the efficiency of some rhodium complexes decrease in the order $\text{RhX}(\text{PPh}_3)_3$, $\text{X} = \text{Cl} > \text{Br} > \text{I} > \text{RhClCO}(\text{PPh}_3)_2 \approx \text{RhH}(\text{CO})(\text{PPh}_3)_3$, and ligands in these complexes $\text{P}(\text{C}_6\text{H}_{11})_3 > \text{PMe}_2\text{Ph} > \text{PMePh}_2\text{PPh}_3 > \text{P}(\text{On}-\text{Bu})_3 > \text{P}(\text{OPh})_3 \gg \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$. In the addition of Me_3SiH and $(\text{EtO})_3\text{SiH}$ to styrene, the order of activity was $\text{RhCl}(\text{CO})(\text{PPh}_3)_2 > \text{RhH}(\text{CO})(\text{PPh}_3)_3 \approx \text{RhX}(\text{PPh}_3)_3$ ($\text{X} = \text{Cl} \gg \text{I}$). With styrene, the yield of 1-silyl-1-phenylethane relative to 2-silyl-1-phenylethane increased with increasing electronegativity of substituents on silicon, $\text{Me} < \text{EtO} < \text{Cl}$. This conclusion might also be reached from the data in Table VIII (Section IV) from use of a platinum catalyst. The relative yields of the two products were not greatly influenced by different phosphine ligands. A surprising amount of ethylbenzene (5–13%) was produced in these experiments.

All the rhodium catalysts gave exclusively *n*-hexylsilanes from 1-hexene, but if the catalysts was used at about 10^{-4} molar ratio to reagents in benzene, no isomerization of the hexene was observed. A polar coordinating solvent such as tetrahydrofuran drastically reduced the rate of hydrosilation. The rhodium complexes were recoverable unchanged after completion of the reactions.

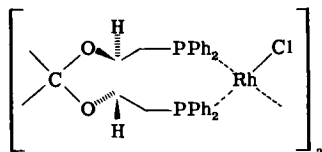
Only Me_3SiH reacted at room temperature and then very slowly. With $\text{RhCl}(\text{PPh}_3)_3$, Me_3SiH reacted 82% in 15 minutes at 50°C ; $(\text{EtO})_3\text{SiH}$, 64% at 100°C in 2 hours; Cl_3SiH , 68% at 120°C in 2 hours. Excess Ph_3P suppressed addition of trimethylsilane to 1-hexene, but it had very little effect upon the rate of addition of triethoxysilane (41). Even in cases where excess free ligand suppressed hydrosilation by Me_3SiH , a trimethylsilylrhodium(III) complex was thought to form because the solution turned the typical yellow color characteristic of $\text{Me}_3\text{Si}-\text{RhHCl}\cdot\text{L}_2$. It seems most likely that excess ligand formed $\text{Me}_3\text{SiRhHClL}_3$ and excluded 1-hexene from the coordination sphere of rhodium, thus suppressing hydrosilation.

Recently, various rhodium carbene complexes were investigated as catalysts for hydrosilation of olefins, acetylenes, and dienes to see whether carbene ligands modify catalytic activity. All reactions were

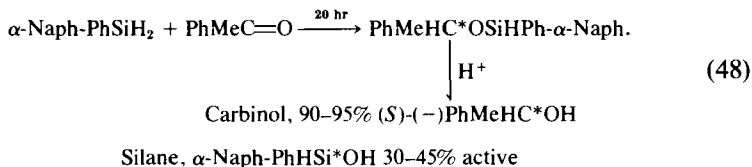
carried out with about 1 mol% catalyst at 100°C for 8 hours. No attempt was made to study rate of reaction or to maximize yields (41). No dramatic effect could be seen for the carbene ligands. Additions to 1-octene were comparable with results from Svoboda *et al.* (37) with 1-hexene.

The addition of triethylsilane to 1-hexyne led to an 80/20 mixture of *cis*- to *trans*-1-triethylsilyl-1-hexene. This is most anomalous; usually, only *trans* isomers result by *cis*-addition of Si—H to the triple bond.

Asymmetric catalysis by chiral rhodium complexes in both hydrogenation and hydrosilation have been found. Kagan (42) recently reported that the chiral phosphine rhodium complex $[(-)\text{-DIOPRhCl}]_2$ gave the most efficient asymmetric syntheses observed to date. This complex is:



At room temperature, this catalyst with an acetophenone-to-catalyst ratio of 100/1 gave results indicated in Eq. (48):



Ojima (43) used the same DIOPRh catalyst earlier to add Et_2SiH_2 , PhMeSiH_2 , Ph_2SiH_2 and $\alpha\text{-naph-PhSiH}_2$ to α -ketoesters to synthesize optically active α -hydroxy carboxylate esters. With diethyl- or phenyl-methylsilane and propyl pyruvate, a double hydrosilation occurred to chiefly make a cyclic product with double asymmetry.

Kumada (44) showed that chiral ferrocenyl phosphine ligands on rhodium gave good optical yields of carbinols from prochiral ketones.

IV

EFFECTS OF THE STRUCTURE OF THE SILANE

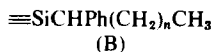
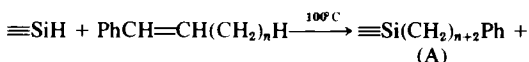
Very little has been done to investigate the effect of the structure of the $\equiv\text{SiH}$ compound in determining the structure of the end products of hydrosilation. Examples can be found, in addition to many that have already been mentioned, which indicate that the structure of $\equiv\text{SiH}$ com-

pound can play a very important role in determining the position of the Si—C bond in the alkyl groups formed by hydrosilation.

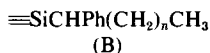
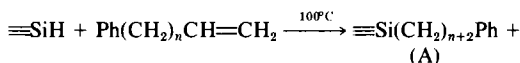
The addition of $\text{Cl}_x\text{Me}_{3-x}\text{SiH}$ ($x = 3, 2, 1$) to phenylalkenes: with chloroplatinic acid frequently formed two adducts (2*h*). (a) $\text{Ph}(\text{CH}_2)_{n+2}\text{SiCl}_x\text{Me}_{3-x}$ and (b) $\text{PhCH}(\text{SiCl}_x\text{Me}_{3-x})(\text{CH}_2)_n\text{CH}_3$. Pike (45) claimed that no (b) formed in the presence of a small amount of an electron-donating solvent such as tetrahydrofuran. 1-Phenylalkenes gave results summarized in Table VI.

The kinetics of addition of Cl_3SiH at 100°C to $\text{Ph}(\text{CH}_2)_2\text{CH}=\text{CH}_2$ in a ratio of 1/1 was examined. A plot of Cl_3SiH vs. time showed that Cl_3SiH disappeared at a constant rate until more than 80% was reacted. The process thus seemed to be of zero order in silane. In 8 minutes, 4-phenyl-1-butene was converted to about 21% *cis*-1-phenyl-1-butene, 67% 4-phenylbutyltrichlorosilane, 10% 1-phenylbutyltrichlorosilane, and about 2% *n*-butylbenzene, which remained constant thereafter. After about 6.5 hours, 99.2% of the Cl_3SiH had reacted. About 2% of the original olefin was then converted to *trans*-1-phenylbutene and 2% to *n*-butylbenzene. The adducts were 4- and 1-phenylbutylsilanes in a ratio of 2.25/1. The influence of structures and ratios of reagents was studied further (see Table VII). MeF_2SiH was bubbled into styrene at $50^\circ\text{--}90^\circ\text{C}$ until 58% of the styrene had reacted to form 2-phenylethyl and 1-phenylethyldifluoromethylsilanes in a ratio of 37/63, indicating that MeF_2SiH tends to make much more 1-phenylethyl product than does any of the chlorosilanes. Excess olefins in the examples of Table VII were recovered almost exclusively as *trans*-1-phenylalkene.

TABLE VI
ADDITION TO 1-PHENYLALKENES



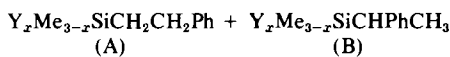
Olefin <i>n</i>	Silane	Olefin/silane	Hours (100°C)	A/B
1	MeCl_2SiH	.8	1	49/51
2	$\text{Me}_2\text{Cl SiH}$	1.5	2	43/57
2	MeCl_2SiH	1.4	2	39/61
2	Cl_3SiH	1.4	2	23/77
4	$\text{Me}_2\text{Cl SiH}$	1.0	66	37/63
4	MeCl_2SiH	1.0	21	32/68
4	Cl_3SiH	1.0	24	10/90

TABLE VII
 ADDITION TO ω -ALKENYLBENZENES


Olefin/SiH	A/B		
With $n = 0$	Me_2ClSiH	MeCl_2SiH	Cl_3SiH
36		65/35	
1.8	84/16	61/39	63/37
1.0	85/15	69/31	57/43
0.45	86/14	67/33	57/43
0.23		61/39	
With $n = 1$			
1.6	100/0	100/0	78/22
0.4	95/5	89/11	67/33
With $n = 2$			
1.4	100/0	100/0	82/18
0.35	98/2	91/9	70/30

A series of compounds, $\text{Y}_x\text{Me}_{3-x}\text{SiH}$, was used to study the influence of X and Y on the ratio of the 1- and 2-phenylethyl silanes. The results are in Table VIII (2*h*). Substituents on the aromatic ring also influence the distribution of adducts. [See Table IX (2*h*)]

Only one example was found in which a silicon compound with the structure $\equiv\text{SiH}_2$ was added to internal olefins with a homogeneous catalyst, and it gave surprising results (46). Dichlorosilane was added to 2-

 TABLE VIII
 $\text{Y}_x\text{Me}_{3-x}\text{SiH} + \text{PhCH}=\text{CH}_2 \longrightarrow$


X	Mol% A		
	Y = Cl	Y = $-\text{OSiMe}_3$	Y = F
0	95	95	95
1	85	75	47
2	68	85	39
3	60	95	

TABLE IX

$$\equiv\text{SiH} + \text{RCH}=\text{CH}_2 \xrightarrow{100^\circ\text{C}} \equiv\text{SiCH}_2\text{CH}_2\text{R} + \equiv\text{SiCHRCH}_3$$

(A) (B)

R	Mol% A	
	With MeCl_2SiH	With Cl_3SiH
C_6H_5-	69	57
$2\text{-ClC}_6\text{H}_4-$		96
$4\text{-ClC}_6\text{H}_4-$		68
$4\text{-BrC}_6\text{H}_4-$	72	68
C_6F_5-	100	100
$2,4,5\text{-Cl}_3\text{C}_6\text{H}_2-$	100	100
$2,6\text{-Me}_2\text{C}_6\text{H}_3-$	100	100
$4\text{-MeC}_6\text{H}_4-$	64	100

butene, 2-pentene, 2-hexene, 3-hexene, and 2-heptene with chloroplatinic acid at temperatures of 72°–150°C. The additions were very slow relative to those with Cl_3SiH , for example, but they gave secondary alkylsilanes in excellent yields, which was unexpected. 2-Hexene reacting for 8 hours at 140°C, gave in 89% yield a mixture of 66% 2-hexyl- and 34% 3-hexyldichlorosilane. 3-Hexene, after 8 hours at 150°C, gave a 56% yield of 3-hexyldichlorosilane. 2-Pentene, reacting for 8 hours at 130°C, gave in 92% yield a mixture of 69% 2-pentyl- and 31% 3-pentyldichlorosilane. 2-Butene is said to have given a small amount of *n*-butyldichlorosilane if it was used "at lower temperatures."

These unusual results suggest that dichlorosilane may have added to these alkenes by a thermal or free-radical mechanism, and that the addition was not catalyzed by chloroplatinic acid in the usual way. No experiment in which these reagents were heated in the absence of platinum was described. *sym*-Tetramethyldisiloxane added to 3-heptene at reflux with chloroplatinic acid in mole ratios of 1/2.1/10⁻⁵ at reflux for 48 hours to give an excellent yield of a mixture of 1,3-diheptyltetramethyldisiloxanes. The heptyl substituents were mostly *n*-heptyl, but they included a considerable amount of 3- and 4-heptyl as well. No 2-heptyl substituents were detected (2a).

sym-Tetramethyldisiloxane and 1-hexene gave almost exclusively di-*n*-hexyldichlorosilane, but 2-hexene and 3-hexene gave mixtures containing 2- and 3-hexyl substituents. These experiments, carried out in sealed tubes at 100°C for 2 weeks or longer, showed that all the olefins isomerized and gave 1-, 2-, and 3-alkyl derivatives in the following re-

spective percent yields: 3-hexene, 76, 10, 14; 2-hexene, 88, 7, 5; 1-hexene, 99, trace.

Andrianov *et al.* (47) studied the addition of a series of disilazanes, $(\text{HSiMe}_2)_2\text{NR}$ ($\text{R} = \text{H, Et, i-Bu, Ph, PhCH}_2, p\text{-NO}_2\text{C}_6\text{H}_4$), to allyldiethylamine in anisole at concentrations of silazane, 1 mole/liter; amine, 2 moles/liter; and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 1×10^{-4} moles/liter. They measured the rate of disappearance of SiH at 45° and at 57°C .

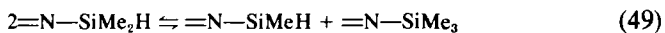
When $\text{R} = \text{H}$, an induction period of about 1 hour was observed, after which addition went slowly to at least 90% completion in 8 hours at 45°C . When $\text{R} = \text{Ph}$ or i-Bu the addition went at nearly the same rate but stopped at 50% conversion at 45°C . With no solvent, with $\text{R} = \text{Ph}$, the reaction was rapid at room temperature and the mixture grew warm in a few minutes. The product was almost exclusively $\text{HMe}_2\text{SiNPhSiMe}(\text{CH}_2)_3\text{NEt}_2$, even if 100% excess allyldiethylamine was present. With $\text{R} = \text{PhCH}_2$, they were unable to get hydrosilation at 80°C .

With $(\text{HMe}_2\text{Si})_2\text{NH}$ and excess allyltrimethylsilane, 20 hours at 80°C brought hydrosilation to completion to make principally $\text{HN}[\text{Me}_2\text{Si}(\text{CH}_2)_3\text{SiMe}_3]_2$. Under the same conditions the N-Ph disilazane and allylaminotrimethylsilane went 48% to completion. After 20 hours at 160°C , all Si-H had disappeared and $\text{PhN}[\text{Me}_2\text{Si}(\text{CH}_2)_3\text{SiMe}_3]_2$ formed (47).

The addition of a series of aminosilanes to 1-hexene, 1-pentene, and 2-pentene and to allylaminosilanes was studied (2j). 1-Alkenes gave *n*-alkyl derivatives. The additions were characteristically slow at 100°C . A typical result with 1-hexene and anilindimethylsilane (reaction for 24 hours at 100°C) was 96% yield of anilino-*n*-hexyldimethylsilane. $\text{Me}_2\text{NMe}_2\text{SiH}$, $\text{Et}_2\text{NMe}_2\text{SiH}$, and $n\text{-Bu}_2\text{NMe}_2\text{SiH}$ reacted less than 10% under the same conditions; $(\text{Me}_2\text{N})_3\text{SiH}$ did not react at all.

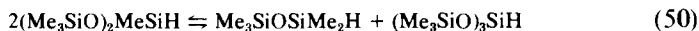
sym-Tetramethyldisilazane and 2-pentene in a mole ratio 1/2, reacting for 40 hours at 100°C , gave a nearly quantitative yield of monopentyl adduct. After 48 hours at 110°C they formed products which were 68% monopentyl and 15.6% dipentyl adducts. These adducts contained 2-pentyl as well as *n*-pentyl products.

Tris-dimethylsilylamine $(\text{HSiMe}_2)_3\text{N}$ and 1-hexene (2j) at 115°C for 72 hours gave a complex mixture. The principal product was $(\text{HexMe}_2\text{Si})_2\text{NSiMe}_2\text{H}$, with some $(\text{HexMe}_2\text{Si})_2\text{NSiMe}_3$, signifying an unexpected redistribution of methyl groups on silicon. Some of this mixture was converted to ethoxysilanes by boiling ethanol. The derivatives included $\text{HexMe}_2\text{SiOEt}$ and Me_3SiOEt as well as $\text{HexMeSi}(\text{OEt})_2$ and $\text{Hex}_2\text{MeSiOEt}$. These products probably arose from a redistribution reaction, such as

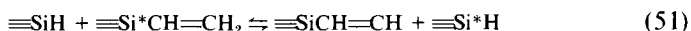


Studies to compare effects of soluble transition metal catalysts on the structure of products obtained from two siloxanes (12b), $(\text{Me}_3\text{SiO})_2\text{MeSiH}$ and $(\text{Me}_3\text{SiO})_2\text{MeSiCH}=\text{CH}_2$, proved this to be a surprisingly complex system. The products depend on the catalyst, but they can be explained as the result of four kinds of reactions:

(a) $\text{Me}_3\text{SiO}-/\text{Me}$ exchange:



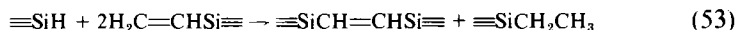
(b) Vinyl/H exchange:



(c) Hydrosilation:



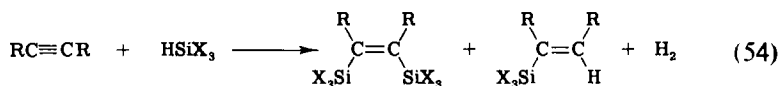
(d) Dehydrogenative double hydrosilation:



No evidence of a redistribution of Me and H groups [Eq. (50)], was observed with these siloxanes. Unsaturated adducts from Eq. (53) showed up; see Table X.

An example of Eq. (53) has been reported (48) in which an equimolar mixture of styrene and triethylsilane with rhodiumbisdimethylglyoximate-triphenylphosphine ($3 \times 10^{-5}\%$) at 90°C for 3 hours gave a yield of 15% *trans*-1-phenyl-2-triethylsilylethylene.

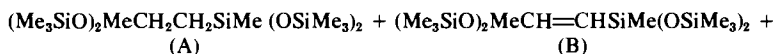
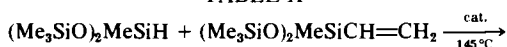
Recently, Kumada *et al.* (49) have published a report on what they refer to as "dehydrogenative, stereoselective *cis* double silylation of internal acetylenes." This appears to be a variation of Eq. (53), with diethyl bipyridyl nickel(II) as the catalyst, in which hydrogen is liberated instead of being added to an alkene to form a saturated product.



R = Et, *n*-Bu, Ph, or Me

X = Cl_3 or Cl_2Me

The surprisingly strong tendency of H_2OsCl_6 to make unsaturated adducts was examined in more detail with different reagents. MeCl_2SiH (1 mole) + $\text{MeCl}_2\text{SiCH}=\text{CH}_2$ (2.5 moles) with $10^{-2} M$ $\text{H}_2\text{OsCl}_6 \cdot 2\text{H}_2\text{O}$ at 120°C for 20 hours gave $\text{MeCl}_2\text{SiCH}_2\text{CH}_2\text{SiMeCl}_2$ (0.87 mole), *trans*- $\text{MeCl}_2\text{SiCH}=\text{CHSiMeCl}_2$ (0.13 mole), and MeCl_2SiEt (0.13 mole). The system $(\text{MeSiO})_2\text{MeSiH}$ (32 mmole); $\text{Me}_3\text{SiCH}=\text{CH}_2$ (40 mmole); $\text{H}_2\text{OsCl}_6 \cdot 2\text{H}_2\text{O}$ (5×10^{-2} mmole) at 100°C for 20 hours gave the following relative amounts (in moles) of products: $\text{Me}_3\text{SiCH}=\text{CHSiMe}(\text{OSiMe}_3)_2$,

TABLE X^a

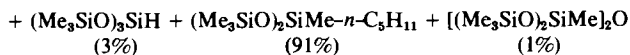
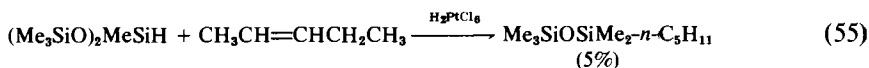
MANY OTHER PRODUCTS FROM EQS. (51) AND (52)

Catalyst	% Conversion of ≡SiH	A/B	Identified by-products
H ₂ PtCl ₆	~100	No B	Almost none
1% Pt/C	~100	99/1	(Me ₃ Si) ₂ O
H ₂ OsCl ₆ ·2H ₂ O	~100	100/931	Ten by-products 21% (Me ₃ SiO) ₂ MeSiCH ₂ CH ₃
RhCl ₃ ^b	~100	No B	Almost none
5% Rh/C	~100	100/7.5	
5% Rh/Al ₂ O ₃	~100	100/5.3	
RuCl ₃	~100	100/20	
Ru/C	~90	100/455	
Ru/Al ₂ O ₃	~65	100/809	
H ₂ IrCl ₆	~100	Multitude of products	
5% Ir/C	~100	100/212	Nine by-products
5% Ir/Al ₂ O ₃	~100	100/144	Nine by-products
5% Pd/C	~0	100/0	
5% Pd/Al ₂ O ₃	~5	100/14	
5% Re/C	~30	100/159	
5% Re/Al ₂ O ₃	~50		

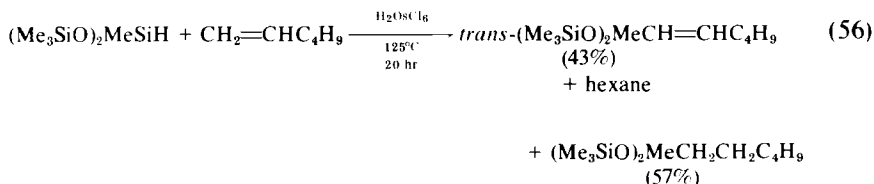
^a From Cheng (12b).^b After 35 days at room temperature there was no reaction. After these 35 days, 24 hours at 100°C gave 3% (A); 24 hours at 120°C gave 98% (A); and 4 hours at 125°C gave 98% (A).

100.0; Me₃SiCH₂CH₂SiMe(OSiMe₃)₂, 12.7; (Me₃SiO)₂MeSiCH=CHSiMe(OSiMe₃)₂, 66.8; Me₃SiCH=CHSiMe₃, 32.4; (Me₃SiO)₂SiMeEt, 72.9; Me₃SiEt, 113; Me₃SiCH₂CH₂SiMe₃, 4; and two unidentified products, small.

The redistribution reaction of Eq. (50) is not restricted to systems containing vinylsiloxanes. It was also observed with 2-pentene as follows:



The formation of 1,2-disubstituted ethylenes is not unique to vinylsilanes.



Under very similar conditions, 2-pentene gave less than 10% conversion to what appeared to be the analogous products. $(\text{Me}_3\text{SiO})_2\text{MeSiH}$ (5 mmoles), styrene (10 mmoles), $\text{H}_2\text{OsCl}_6 \cdot 2\text{H}_2\text{O}$ (10^{-3} mmole) at 20 hours at 140°C gave a 97% yield of $\text{trans}-(\text{Me}_3\text{SiO})_2\text{MeSiCH}=\text{CHPh} + \text{PhEt}$. At 120°C and 20 hours, a 26% yield of about a 50/50 mixture of this product mixed with $(\text{Me}_3\text{SiO})_2\text{MeSiCH}_2\text{CH}_2\text{Ph}$ was obtained. The yield of unsaturated adduct was increased by higher temperatures.

Chloroiridic acid in Table X gave an amazing mixture of products. Investigation of these showed that this catalyst is remarkably effective at temperatures above about 125°C at bringing about the redistribution of substituents on the silicon atom bearing an SiH bond. No unsaturated compound need be present. Equilibria a step beyond that of Eq. (50) became important:



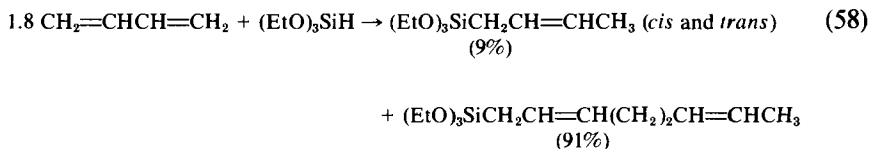
$(\text{Me}_3\text{SiO})_2\text{MeSiH}$ (200 g) was heated to reflux under a small fractionating column. One ml of a 1% by wt. solution of Ir as H_2IrCl_6 in absolute ethanol was added. The mixture was slowly distilled until the temperature of the reflux was 118°C . Low boiling products were condensed in a dry ice trap. Analysis indicated the wt% distribution obtained in this way to be approximately: Me_3SiH , 23%; $\text{Me}_3\text{SiOSiMe}_2\text{H}$, 12%; $(\text{Me}_3\text{SiO})_2\text{MeSiH}$, 14% (starting material); and $(\text{Me}_3\text{SiO})_3\text{SiH}$, 51%. With no other catalysts did products such as Me_3SiH appear.

V

STUDIES WITH CONJUGATED DIENES

The hydrosilation of butadiene, isoprene and other simple conjugated dienes with platinum catalysts has not been intensively studied. It usually occurs by 1,4 addition and only at elevated temperatures (10). Although palladium catalysts are practically ineffective to hydrosilate an alkene, they are very active under mild conditions with conjugated dienes to give two principal products, sometimes in 100% yields. With triethoxysilane, butadiene, and $\text{PdCl}_2(\text{PhC}\equiv\text{N})_2$ (5.5×10^3 moles/mole) at 22°C for 24

hours, for example (50),

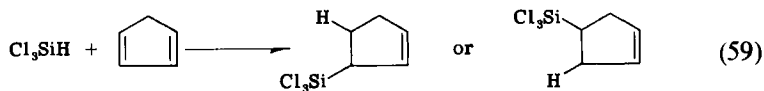


The yield of 1:1 adduct rose to about 85% if the reaction was carried out at about 100°C with $[\text{PdCl}-\pi\text{-C}_3\text{H}_5]_2$ as the catalyst.

Not only do palladium complexes catalyze reactions of Eq. (58), but nickel complexes were also effective (51) and formed the same products. Complexes such as $\text{Fe}(\text{CO})_5$ and $\text{Fe}_2(\text{CO})_8$ were ineffective. Cobalt carbonyl, and tris-triphenylphosphinerhodium chloride were effective even at room temperature, but no 2:1 adducts were made. With both palladium and nickel, the activity of the catalyst and the distribution of products between 1:1 and 2:1 adducts is greatly dependent on the nature of the donor ligands on the metal.

These studies were extended to hydrosilation of cyclopentadiene with trichlorosilane (52). This is most difficult with platinum catalysts. Palladium complexes favored production of 1:1 adducts as a mixture of 3- and 4-trichlorosilylcyclopentene. Nickel complexes produced substantial amounts of 1:2 adducts as trichlorosilyl-substituted 4,7-methylene-4,7,8,9-tetrahydroindanes, with the exception of nickel tetracarbonyl, which was very active and selectively formed almost exclusively 3-trichlorosilylcyclopentene with no 1:2 adduct.

The 1:2 adducts in these examples were accounted for by dimerization of cyclopentadiene and subsequent hydrosilation of dicyclopentadiene. The 3-trichlorosilyl isomer is that expected from 1,4 addition of trichlorosilane. Unless isomerization occurred, the 4-isomer could arise only by 1,2 addition



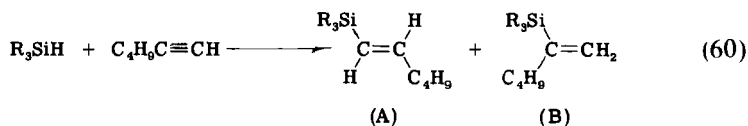
Andrianov *et al.* (52) studied the rate of disappearance of Si—H as a function of time, temperature, and concentration of chloroplatinic acid in an equimolar solution of isoprene and dodecamethylhexasiloxane, $\text{H}(\text{Me}_2\text{SiO})_5\text{SiMe}_2\text{H}$. With a constant concentration of catalyst a plot of % conversion of SiH up to at least 60% vs. time at 20°, 50°, 70° and 110°C gave a family of straight lines. The slopes of the lines increased by a factor of 2.5–3 between 50° and 110°C.

A linear relationship between % SiH and time suggests pseudo-zero-order kinetics, in which the rate of reaction appears to be independent of the concentrations of isoprene and siloxane. A plot of % conversion of SiH vs. concentration of catalyst at 110°C for 5 hours also gave a straight line, indicating that the rate of reaction is directly proportional to concentration of catalyst, i.e., first-order in catalyst.

VI

HYDROSILATION OF ACETYLENES

Pukhnarevich *et al.* (53) showed that the structure of silanes, R_3SiH (in which R_3 was 15 combinations of $R = Me, Et, n\text{-}Pr, i\text{-}Pr, i\text{-}Bu, Me_3SiO\text{---}, ClCH_2, EtO, i\text{-}PrO,$ and Ph) had very little effect on the ratio of isomeric adducts that form by their addition to 1-hexyne with chloroplatinic acid according to Eq. (60).



The β -adduct **B** was favored in every instance. The ratio of **A/B** varied from 1/1 for $Me(Me_3SiO)_2SiH$ to 1/5 for $Me_2Me_3CCH_2SiH$, but no identifiable trend could be discerned for electronic or steric effects on the **A/B** ratios.

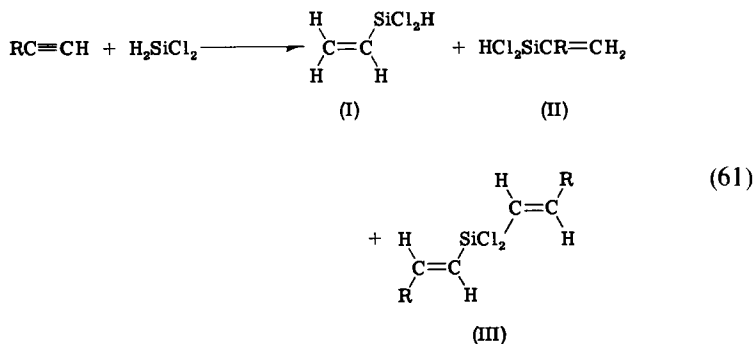
The effect of solvents on the kinetics of addition to hexyne-1 was studied (36) with Et_3SiH . Solvents with dielectric constants from 1.6 to 20.7 had scarcely any measureable effects on the rates of addition. Electron-donating solvents such as pyridine or dimethyl sulfoxide even in very small amounts stopped the reaction entirely.

The effect of R in $RC\equiv CH$ on rate of reaction was found (54) to be slight despite large differences in the inductive, steric, and conjugative characteristics of about ten widely differing R groups.

Benkeser *et al.* (55) showed that a mole ratio of $2Cl_3SiH$ to 1-hexyne would react completely in a long time. In 24 hours, a 98% yield of mono-adducts had formed. After 111 hours, the same mixture yielded 20% 1,6- and 18% 1,2-bistrichlorosilylhexane. By increasing the concentration of catalyst, the yield of these two diadducts was increased to 44% and 40%, respectively. In this work, 1-trichlorosilyl-1-hexene behaved very much like 1-phenyl-1-hexene, shown in Table VI to form 1,6-diadducts.

Benkeser and Ehler (56) studied the addition of dichlorosilane to five

acetylenes with chloroplatinic acid, platinum on carbon, and with benzoyl peroxide. Dichlorosilane at room temperature undergoes exclusively *cis* addition with chloroplatinic acid with the silane/acetylene ratio = 2/1.



Platinum on carbon did almost exactly the same thing but required a temperature of about 100°C to do so. With excess acetylene, only **III** formed. With *tert*-butylacetylene no **II** formed, probably because of steric hindrance, but **I** and **III** formed readily. 3-Hexyne reacted more slowly, required heat with chloroplatinic acid, and formed exclusively *cis*-3-dichlorosilyl-3-hexene. Trichlorosilane with platinum on carbon also added (57) to 1-alkynes or to phenylacetylene exclusively by *cis* addition to give only *trans* adducts. Later works (58) indicate that chloroplatinic acid and other soluble catalysts also give exclusively *cis* addition with a wide variety of Si—H compounds.

Free-radical additions of trichlorosilane to acetylenes initiated by benzoyl peroxide were stereospecific *trans* additions, giving only *cis* adducts. The same workers observed that tri-*n*-butyl amine also catalyzed addition of trichlorosilane to phenylacetylene but gave a mixture of *cis*- and *trans*-1-phenyl-2-trichlorosilylethene, 1,1-phenyltrichlorosilylethene, and 1-phenyl-1,2-bistrichlorosilylethane (54). No stereospecificity was observable with the amine as catalyst.

A macroreticular styrene-divinylbenzene copolymer substituted with cyanomethyl groups sorbs chloroplatinic acid from its aqueous solution. The complex containing 1.45% platinum was used to study the kinetics of addition of trichlorosilane to acetylene in the vapor phase at 100°C (59).

The rate seemed to be accelerated by the product, vinyltrichlorosilane. At high conversions, the bed of catalyst became overheated by the strongly exothermic reaction.

The rate was measured with acetylene and trichlorosilane in a ratio of 2/1 at constant space velocity in the bed at 80°, 100°, 120°, and 140°C.

Acceleration of rate by temperature was very small. Conversions at varying space velocities resembled that of a zero-order reaction. If this were really a zero-order process, the energy of activation would be only 4.4 kcal/mole.

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Olefin Metathesis

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E. A. OFSTEAD

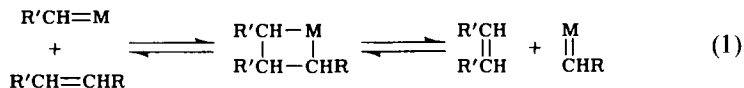
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I

INTRODUCTION

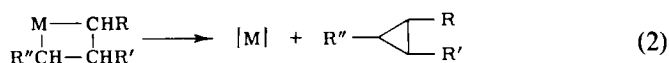
The issue regarding whether olefin metathesis proceeds via a pairwise (1-3) or nonpairwise (4, 5) mechanism appears to be resolved (6-10). Substantial evidence points to a nonpairwise chain mechanism that favors a carbene-bearing metal interacting with an incoming olefin and forming a metallocyclobutane intermediate; said intermediate then rearranges into a different carbene-metal complex, thus forming the new outgoing olefin:



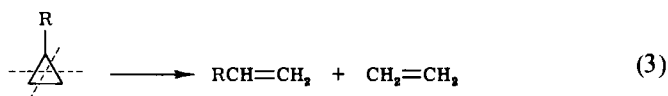
This survey will avoid a redundant recounting of the arguments that support alkylidene scrambling by a nonpairwise scheme (11). Rather, our purpose is to present a "state-of-the-art" account of four vital areas related to olefin metathesis, where significant results have been reported lately. First, if carbene-metal species are indeed involved in the metath-

esis process, there is a need to explain their origins. Because the scope of ingredients used as catalysts for olefin metathesis is extremely broad, encompassing numerous metals in a variety of oxidation states and having different ligand fields, one wonders whether organometallic chemistry is at the verge of discovering a single basic and general reaction wherein an olefin and a metal inevitably tend to combine exclusively to produce a carbene-metal entity. If such a general reaction is fictional, the challenge escalates as one needs to describe a variety of elementary steps that produce the initial carbene-metal for every *individual* class of metathesis catalysts.

Second, several investigations have implied that the formation of cyclopropanes is related to olefin metathesis (5, 12, 13). Extrication of the metal from the metallocyclobutane intermediate has been suggested (5) as a route to the three-membered ring:



However, the generation of cyclopropane derivatives was also shown to implicate an alternate route not requiring a metallocyclobutane transition state (14). In addition, a metathesis catalyst successfully converted certain cyclopropanes to metathesis-related olefins by way of a carbene elimination process (15-17), according to Eq. (3).



It remains unanswered whether observed cyclopropanations and carbene retroadditions [Eq. (3)] always share a common transition state with olefin metathesis.

Third, it is acknowledged that the metathesis step itself is responsible for the formation of both *cis* and *trans* vinylene configurations (18). The steric course in olefin metathesis has been scrutinized by several researchers. Two basic phenomena are recognized:

(a) Marked stereospecificity in the metathesis of acyclic olefins is rare. In most cases, reactions proceed to equilibrium; any observed initial stereospecificity is obscured as reactions proceed to the thermodynamically predicted *cis/trans* composition (19).

(b) In contrast, stereospecificity can be maintained in certain cycloolefin metathesis reactions by proper choice of catalyst combinations (20-22).

Finally, substantial progress has been recorded in recent years in ex-

panding the synthetic applications of olefin metathesis. In particular, hardy catalysts capable of withstanding polar environments have been developed, facilitating metathesis of olefins possessing certain polar functionalities (23, 24). Most significant advances in this area were achieved in polymer syntheses. Cycloolefins possessing halogen, ester, ether, nitrile, or anhydride substituents were polymerized by ring-opening, leading to new functional polymers.

II

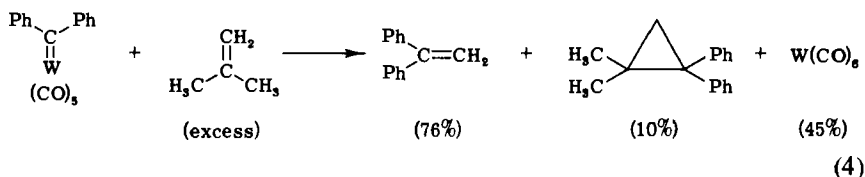
ORIGINS OF CARBENE-METAL COMPLEXES

Transition metals in Groups IVA–VIII A have been claimed to exhibit metathesis catalytic activity (25). The heavier metals, in the fifth and sixth periods of the periodic table, are more prone to effect metathesis than their counterparts of the fourth period. The elements that demonstrate highest activity are tungsten, molybdenum, and rhenium. Procedures employed in the preparation of catalyst systems are diverse in many respects. For example, tungsten-based catalysts can be prepared from precursor compounds ranging from W(0) to W(VI) oxidation states. For the most part, cocatalysts are required; the composition of the ligand field surrounding the metal is not very restricted. (Nevertheless, the ligand field does affect specific catalyst features, such as overall efficiency, capacity to metathesize certain substrates, stereospecificity, and retention of activity in polar environments.)

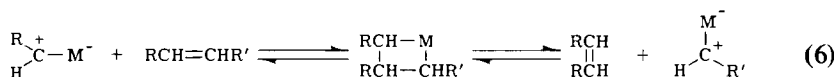
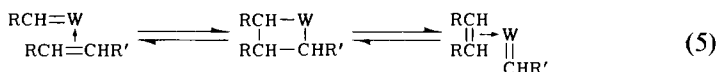
For the purpose of examining potential routes to the formation of the initial carbene-metal entity, it is convenient to classify catalysts into three major, albeit rather arbitrary, categories. The first group comprises catalyst systems utilizing a relatively stable and well-characterized carbene which is attached to the metal. The second class consists of systems that are activated by organometallic cocatalysts which presumably form σ -bonded R—M transients, wherein M is the transition metal. The third category includes catalyst combinations that do not involve a prior carbene or an organometallic component.

A. Catalysts Possessing Stable Carbene-Metal Ligands

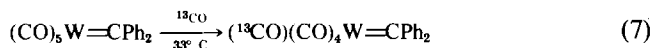
Following Casey's experiment (5) depicted in Eq. (4), Katz and co-workers (26, 27) demonstrated that the stable W(0) carbene complex $(\text{CO})_5\text{W}=\text{CPh}_2$ may also be employed as a metathesis catalyst.



In comparison with other catalysts, (diphenylcarbene)tungstenpentacarbonyl is surprisingly sluggish (26). This observation is significant as it relates to diverse views regarding the carbene-to-metalcyclobutane interconversion. Whereas Casey emphasizes a need to accommodate the incoming olefin within the coordination sphere of the metal prior to rearrangement to a metallocycle [Eq. (5)], Katz (28) has described the process essentially as a dipolar attack of a polarized carbene-metal ($\text{R}_2\text{C}^+-\text{M}^-$) on the olefin [Eq. (6)]. The latter does not specify a need for π -complexation of the olefin as a precondition to metathesis.



Hence, Casey's scheme calls for an empty coordination site on the metal in addition to the complexed carbene. Recently, Casey demonstrated that carbonyls of $(\text{CO})_5\text{W}=\text{CPh}_2$ are vulnerable to exchange processes under relatively mild reaction conditions (29):



At low temperatures, under conditions where carbonyl exchange is suppressed, the highly reactive $(\text{CO})_5\text{W}=\text{CHPh}$ did not exhibit any carbene exchange of the type in Eq. (4). Rather, the reaction products indicated a direct electrophilic attack on the olefin by the carbene. (The exclusive formation of cyclopropanes will be detailed in Section III.)

These results render support to the supposition that the metallocyclobutane transition state which provides for metathesis is produced by an internal rearrangement of the complexed carbene and olefin substrates, as depicted in Eq. (5).

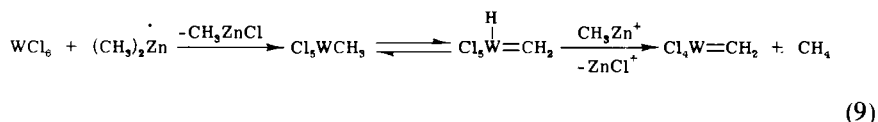
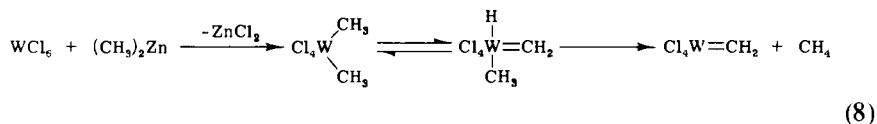
As pointed out elsewhere (30-32), the relevance of ligand exchange to the logistics aspects of olefin metathesis is enormous. It has been speculated that a major contributor to the inefficiency of $(\text{CO})_5\text{W}=\text{CPh}_2$ as a metathesis catalyst is the slow rate of displacement of carbonyl ligands.

This hypothesis is supported by Chauvin's report (33) on a catalyst derived from $(\text{CO})_5\text{W}=\text{C}(\text{OEt})\text{C}_4\text{H}_9$. This highly stable carbene-W(0) compound does not display catalytic activity for cyclopentene monomer. When mixed in the dark with TiCl_4 , a slow evolution of 1 equivalent of CO occurs. Subsequent thermal or photochemical activation produces an extremely efficient catalyst system. Chauvin demonstrated that a high conversion to polypentenamer is obtainable at a W/cyclopentene ratio of 10^{-6} at 5°C . The role of TiCl_4 is not well understood; nevertheless, it promotes carbonyl displacement which appears to be essential.

Highly strained cycloolefins, such as norbornene and cyclobutene, have been reported (34) to undergo slow metathesis using $(\text{CO})_5\text{W}=\text{CPh}_2$.

B. Catalysts Activated by Organometallic Cocatalysts

It has been well documented that organometallic cocatalysts do provide σ -bonded alkyl groups when reacted with transition metal derivatives, particularly when the transition metal is at a high oxidation state. Typical examples of active catalyst systems are unmodified and alcohol-modified $\text{WCl}_6/\text{R}_m\text{AlCl}_n$ ($m + n = 3$), WCl_6/RLi , $\text{WCl}_6/\text{R}_4\text{Sn}$, $\text{WCl}_6/\text{R}_2\text{Zn}$, $\text{MoCl}_5/\text{R}_3\text{Al}$, and $\text{Mo}[(\text{Ph}_3\text{P})_2\text{Cl}_2(\text{NO})_2]/\text{R}_3\text{Al}_2\text{Cl}_3$. Carbene-metal generation from σ -bonded alkyl groups was first proposed by Muetterties (35, 36) when he observed CH_4 generation by reacting $(\text{CH}_3)_2\text{Zn}$ with WCl_6 . Muetterties' schemes are presented in Eqs. (8) and (9).



The $\text{CH}_3-\text{W} \rightleftharpoons \text{CH}_2=\text{W}-\text{H}$ equilibrium, proceeding by α -hydrogen migration from the σ -alkyl to the metal, has been demonstrated by Green (37). Abstraction of α -hydrogens as a route to isolable alkylidene-tantalum complexes was reported by Schrock (38, 39). Additional evidence that carbenoid species are formed in reactions of $(\text{CH}_3)_3\text{Al}_2\text{Cl}_3$ and $\text{Mo}[(\text{Ph}_3\text{P})_2\text{Cl}_2(\text{NO})_2]$ as well as $(\text{CH}_3)_4\text{Sn}$ and WCl_6 has been recently reported by Grubbs (40). Reaction of the selected transition metal compound with the appropriate organometallic cocatalyst afforded methane

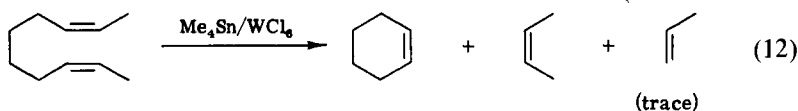
and ethylene. Perdeuterated methane and ethylene were produced when the cocatalyst was $(\text{CD}_3)_4\text{Sn}$:



The suggested scheme for ethylene formation is dimerization of methylene-metal complexes:

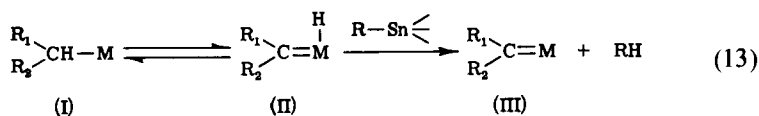


Evidence for a methylene-metal-initiating species was provided by detection of propylene early in the course of metathesis of 2,8-decadiene with $\text{Me}_4\text{Sn}/\text{WCl}_6$, in addition to normal metathesis products:

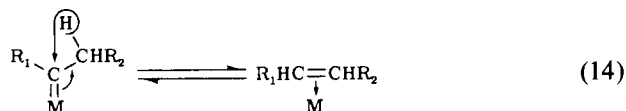


Proper deuterium-labeling experiments involving $(\text{CD}_3)_4\text{Sn}$ and [1,1,1-, 10,10,10- D_6]-2,8-decadiene confirmed that propylene is indeed the first-formed olefin, and its structure indicated that the methyldiene and ethyldiene moieties originated from Me_4Sn and 2,8-decadiene, respectively.

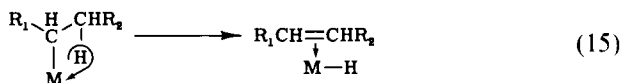
In view of the possibility of α -hydrogen transfer to metal, it remains possible that the metathesizing carbene complex has structure **II** rather than **III** [Eq. (13)]:



The observed methane generation points to a plausible **I** \rightarrow **III** or **II** \rightarrow **III** transformation, but it does not distinguish which of the structures (**II** or **III**) is the metathesis-active carbene. This matter is mechanistically significant with regard to the chain termination process. Type **III** may terminate by a bimolecular dimerization sequence as in Eq. (11), or it may convert to a π -olefin complex via an uncommon 1,2-hydride shift:

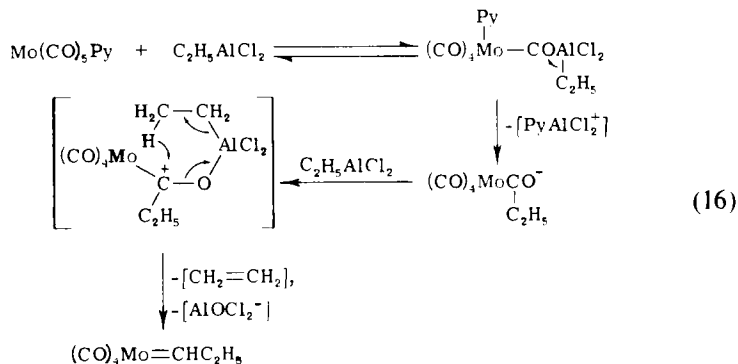


Type **II** may deactivate simply by reverting back to a σ -alkyl (**I**), followed by termination via a Ziegler route, namely halogen abstraction from a metal, or rearrangement to a π -olefin complex according to Eq. (15):



Strong arguments in favor of hydride-metal involvement in the generation of carbene-metal complexes are comprehensively presented in Rooney's monograph on olefin metathesis (41). Spectral evidence has been presented for existence of M—H groups in (a) systems utilizing Ir, Ru or Os, which metathesize highly strained cyclic substrates (42), and (b) the widely used $\text{RAlCl}_2/\text{WCl}_6/\text{ROH}$ catalyst (43). The conclusion of Rooney's work is that the role of the hydride is to isomerize olefin reversibly to carbene complexes via a σ -alkyl metal intermediate, thus supporting type II carbene-metal complex. This proposal is attractive in that it links olefin metathesis to other transition metal-catalyzed reactions of olefins, such as dimerization and polymerization, where the reacting intermediate is the σ -alkyl group.

An alternate route to carbene generation has been proposed for the $\text{RAlCl}_2/\text{Re}(\text{CO})_5\text{Cl}$ and $\text{RAlCl}_2/\text{Mo}(\text{CO})_5\text{Py}$ systems (44–46). The key step in this route is insertion of a CO ligand in the $\text{R}-\text{AlCl}_2$ followed by a sequence of steps that produce the initial carbene. Equation (16) demonstrates this proposal.

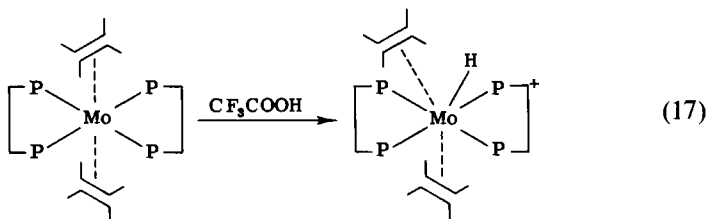


The purpose in offering this rather complicated scheme was to rationalize the presence of minor amounts of 1-butene in the metathesis of 1,7-octadiene, thus requiring existence of a propylidene moiety.

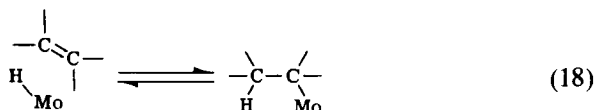
C. Catalysts Void of Organometallic Cocatalysts

Whereas formation of the original carbene-metal species in catalysts from the above two categories is reasonably accountable for and sub-

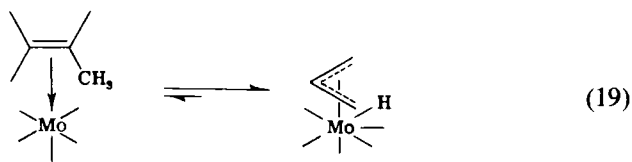
stantiated by experimental work, pathways for carbene formation in systems that do not employ organometallics are in most cases still unresolved. Nevertheless, results of several investigations have been disclosed lately that point to the hydrogen transfer processes in Mo and W complexes with olefins. These may be related to carbene generation in olefin metathesis catalysts. Osborn observed (47) that $\text{Mo}(\text{C}_2\text{H}_4)_2(\text{diphos})_2$, having a trans octahedral structure, undergoes protonation when reacted with CF_3COOH .



NMR studies clearly indicated a rapid and reversible ethylene insertion-deinsertion process, as illustrated in Eq. (18).



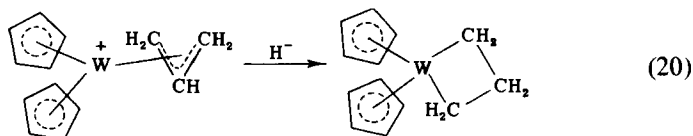
A different reaction occurs when propylene is employed. A π -allyl hydride complex is the observed stable product, thus suggesting the following equilibrium:



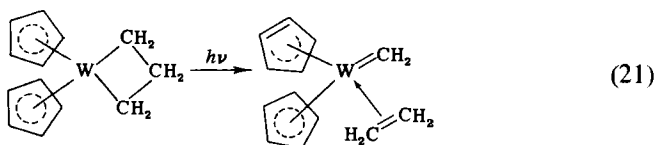
Two significant items were confirmed in this work: (a) Molybdenum, and most probably tungsten, can expand its sphere of coordination beyond 6; and (b) hydride shifts transforming olefins to allyls or π -allyls, via $\pi \rightarrow \sigma$ and $\pi \rightarrow \eta^3$ processes, respectively, are feasible in metals that are known to produce active metathesis catalysts.

Green demonstrated (48) that a π -allyl complexed to W or Mo can undergo a nucleophilic attack by H^- on the central carbon of the η^3 allylic group, forming a stable metallocyclobutane. [See Eq. (20).] Cyclopropane and propylene were evolved (49) on heating the metallocyclic

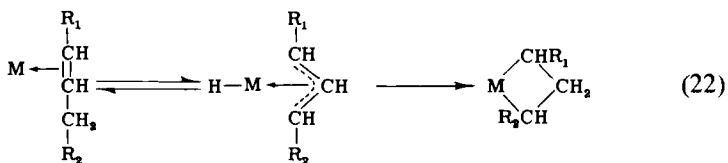
product of Eq. (20). In contrast, irradiation of the complex produced ethylene and some methane. The intermediacy of a carbene-bearing



metal, possessing a π -complexed olefin, has been suggested for the photolytic decomposition of Green's metallocyclobutane.



Osborn and Green's elegant results are instructive, but their relevance to metathesis must be qualified. Until actual catalytic activity with the respective complexes is demonstrated, it remains uncertain whether this chemistry indeed relates to olefin metathesis. With this qualification in mind, their work in concert is pioneering as it provides the initial experimental backing for a basic reaction wherein an olefin and a metal *exclusively* may produce the initiating carbene-metal complex by a simple sequence of π -complexation followed by a hydride shift, thus forming a π -allyl-metal hydride entity which then rearranges into a metallocyclobutane via a nucleophilic attack of the hydride on the central atom of the π -allyl species:



Significantly, this scheme implies that ethylene cannot generate the starting metallocycle; hence, it will be inert to self-metathesis unless there are other routes for generation of the initial carbene. Boelhouwer, who followed the production of $\text{CH}_2=\text{CD}_2$ from $\text{CH}_2=\text{CH}_2$ and $\text{CD}_2=\text{CD}_2$, using $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst (50), found it necessary to preexpose the catalyst to a higher olefin, e.g., propylene or butene-1, before he could appreciably metathesize the ethylenes. Table I summarizes Boelhouwer's results.

$\text{Mo}(\text{CO})_6/\text{Al}_2\text{O}_3$ was found to be inert to self-metathesis of ethylenes

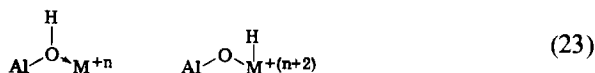
TABLE I
SELF-METATHESIS OF ETHYLENES OVER $\text{Re}_2\text{O}_7/$
 Al_2O_3 ^a

Catalyst preexposure to propylene (min)	Conversion (%)	
	30 min	60 min
0	0	0.5
30	5	11
90	10	19

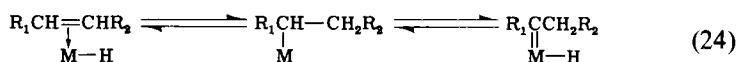
^a Data from Olsthoorn and Boelhouwer (50).

(51) initially; however, this catalyst is known to convert ethylene to propylene directly (52) ($3\text{C}_2 \rightarrow 2\text{C}_3$), and shortly after propylene was detected, ethylene and ethylene- d_4 began to scramble. These findings are in accord with an initiation mechanism involving a metal and an olefin exclusively.

The formation of a metal-hydride entity in supported heterogeneous catalysts has been proposed by Rooney (43). Surface hydroxylic groups on the support provide the needed hydrogen.



Carbene generation is envisioned as being a reversible sequence as depicted in Eq. (24).



The route to carbene initiation for systems catalyzed solely by transition metal salts (53, 54), or their combinations with Lewis acids such as AlCl_3 (55), is not well established. Nevertheless, some evidence suggests reduction of the metal by the olefinic substrate (53). Zero-valent (56) and hexavalent (57, 58) tungsten complexes that promote metathesis when activated by UV radiation are the least-understood metathesis systems.

To summarize, experimental evidence has been advanced regarding hydride involvement in the initiation step of olefin metathesis with certain catalysts. One concept considers the source of the hydride to be external—that is, originating from a promoter or a cocatalyst. A second concept assumes a hydride being generated internally from the metathesizing olefin. It is quite possible that both concepts are operative.

One needs to emphasize that the extent of these hydride shifts, in comparison to the overall reaction, is infinitesimal. Otherwise, gross hydrogen exchanges would have obscured the effectiveness of reported labeling experiments, particularly those which establish the site of scission (59) and the occurrence of regenerative metathesis in terminal olefins (60, 61).

Whether the metal in the metallocycle possesses a hydride atom remains unsolved. This may dictate the route to termination of the chain reaction.

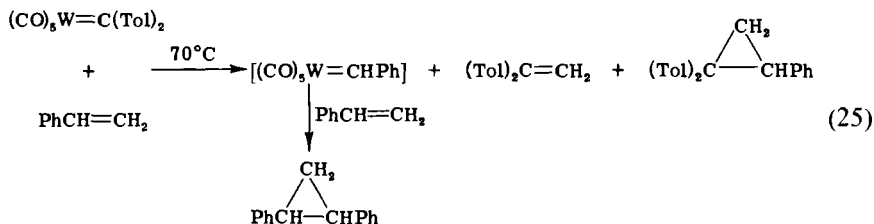
III

CYCLOPROPANATION

As opinions regarding the metathesis reaction pathway have shifted in recent years to favor a nonpairwise carbene-to-metallocyclobutane transformation, increasing attention has been given to the mechanistic significance of cyclopropane \rightleftharpoons olefin interconversions. This interconversion process seems to occur primarily when certain relatively inefficient catalysts are employed, which in itself raises questions. Under ideal conditions, "good" metathesis catalysts are remarkably efficient promoters of transalkylidenation, and consequently are well suited for olefin and polymer syntheses. Thus, most early studies focused primarily on applications. When "side" reactions did occur, they were usually ignored or presumed to be trivial cationic processes.

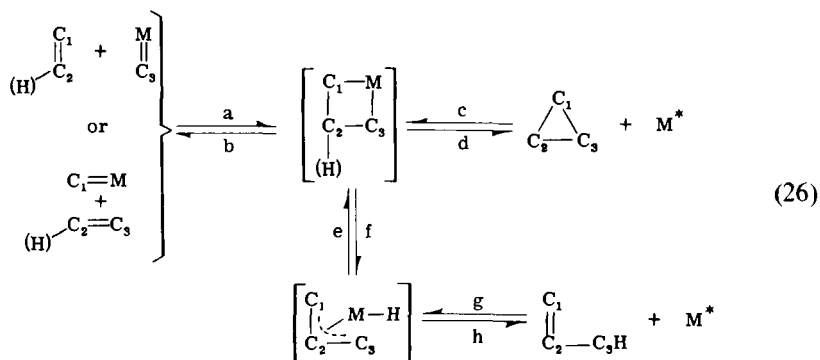
Cyclopropanes in low yield were first noted in 1964 by Banks and Bailey (12) during the disproportionation of ethylene, but little significance was attached to that observation until recently, because such products had no obvious relevance to early mechanistic concepts based on pairwise rearrangements of bisolefin complexes. However, the subsequent adoption of carbenelike species as metathesis intermediates (4) provided a foundation for later development of cyclopropanation concepts. The notable results of Casey and Burkhardt (5) made an impact which seemed rather neatly to unify mechanistically the interconversion of cyclopropanes and metathesis olefins, although the reactions which they observed were stoichiometric rather than catalytic [see Eq. (4)]. Nevertheless, their work indicated a net redistribution of $=CPh_2$ and $=CH_2$ from $(CO)_5W=CPh_2$ and isobutylene, respectively, to form $CH_2=CPh_2$. Dissociation and transfer of CO yielded $W(CO)_6$. Unfortunately, the fate of the isopropylidene moiety remained unknown. In 1976,

Casey extended his work (62) to conclude that a degree of chain-carrying character existed, as implied by diphenylcyclopropane formation. Chain character would be essential in a catalytic process as depicted in Eq. (25).



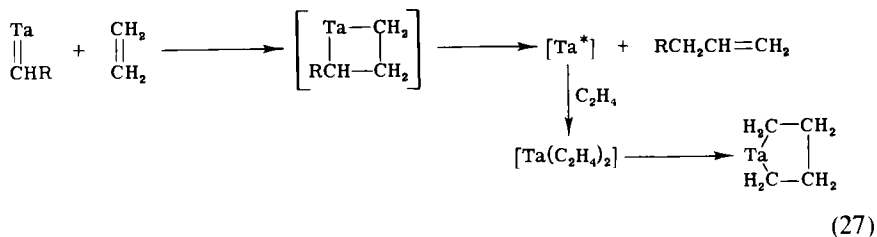
As pointed out in an earlier section, Katz and co-workers demonstrated that Casey's complex, $(\text{CO})_5\text{W}=\text{CPh}_2$, could also be employed to initiate the metathesis of α -olefins (26) as well as the polymerization of certain cycloolefins (27, 63).

Several studies now exist which add credence to Casey's attractive proposal that metallocyclobutanes intervene in metathesis and cyclopropanation reactions. Additionally, metallocyclobutanes have been observed to interconvert to propylene derivatives by way of β -hydrogen transfer reactions. It is not well established, however, whether precoordination of the reacting olefin is required in all these processes. The proposed interrelation of these reactions may be formally presented as follows:



The undefined but presumably coordinatively unsaturated species M^* would likely recombine with a free olefin to form a complex which is not a metathesis-active species, but which would now require an additional

carbene regeneration step to restore metathesis activity. Casey's results (14) suggested the formation of an inactive π complex, $(\text{CO})_5\text{W}(\text{PhCH}=\text{CH}_2)$, via an isomerization process in reactions of the carbene complex $(\text{CO})_5\text{W}=\text{C}(\text{CH}_3)\text{Ph}$, and Schrock found (64) that decomposition of the tantalum carbene $(\eta^5\text{-C}_5\text{H}_5)\text{TaCl}_2[=\text{CHC}(\text{CH}_3)_3]$ in the presence of excess ethylene afforded a transition metal residue consisting of a bisethylene complex which had converted spontaneously to the recovered metallocyclopentane.



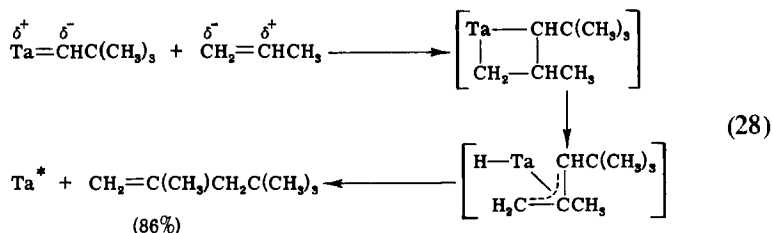
Thus, reactions affording either cyclopropanes or propylenes would most likely represent forms of termination of metathesis activity. As a corollary, any catalytic conversion of cyclopropanes to metathesis olefins via Eq. (26) would seem to require decomposition of the metal-carbene species in order to regenerate a "naked" metal species (M^*) capable of further reactions with cyclopropanes. Of course, bimolecular carbene decomposition to yield an olefin as in Eq. (11) (e.g., ethylene from $2\text{M}=\text{CH}_2$) is one accepted process which could account for regeneration of M^* .

In scrutinizing the various proposed reaction sequences in Eq. (26), one may classify the behavior of carbene complexes toward olefins according to four intimately related considerations: (a) relative reactivities of various types of olefins; (b) the polar nature of the metal-carbene bond; (c) the option of prior coordination of olefin to the transition metal, or direct interaction with the carbene carbon; and (d) steric factors, including effects arising from ligands on the transition metal as well as substituents on the olefinic and carbene carbons. Information related to these various influences is by no means exhaustive at this point. Consequently, some apparent contradictions exist which seem to cast doubt on the relevance of various model compound studies to conventional catalysis of the metathesis reaction, a process which unfortunately involves species which elude direct structural determination.

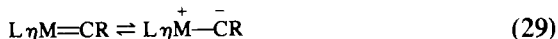
In early studies of the molecular weight-regulating efficiency of various olefins in the metathesis polymerization of cyclopentene, the results of

Pampus and co-workers (65) established the relative reactivity of a series of olefins to be 1-butene > 2-butene > isobutylene. This order of reactivity has been confirmed by others, and exactly parallels the reported order of stability of transition metal (Rh) complexes with these olefins (66), thus clearly implicating precomplexation of the olefin with the transition metal prior to metathesis. On a limited scale, Schrock observed a similar order of reactivity for olefins in reactions with $(\eta^5\text{-C}_5\text{H}_5)\text{TaCl}_2[\text{=CH}(\text{CH}_3)_3]$, which is known to possess a nucleophilic carbene carbon (64). This complex also provides the requisite empty coordination site needed for precomplexation. In that study, cyclopropanes or metathesis olefins were not observed as products.

The fact that Schrock's proposed metallocyclobutanes decomposed to propylene derivatives rather than cyclopropanes was fortunate in that further information resulted regarding the stereochemistry of the olefin reaction with the carbene carbon, as now the β -carbon from the metallocycle precursor retained its identity. The reaction course was consistent with nucleophilic attack of the carbene carbon on the complexed olefin, despite potential steric hindrance from the bulky carbene. Decomposition via pathways f-h in Eq. (26) was clearly confirmed in studies utilizing deuterated olefins (67).

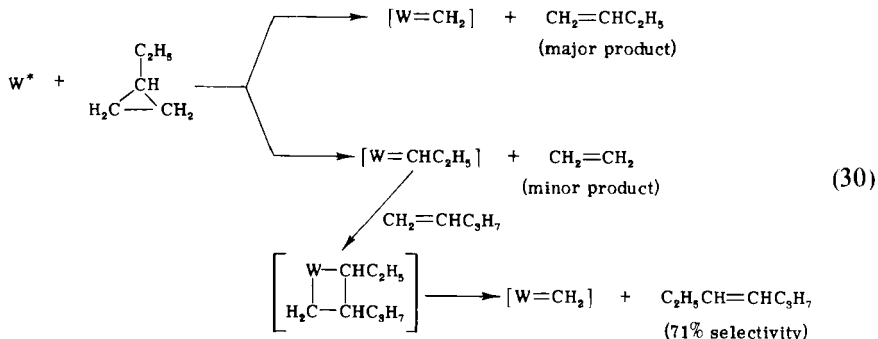


In a significant series of reports describing the formation of metathesis-like products from cyclopropanes via a carbene retroaddition reaction, Gassman (68) also presented results that were interpreted to mean that carbenes which normally participate in conventional metatheses are negatively polarized (nucleophilic).



Previous work had demonstrated the remarkable conversion of cyclopropane to ethylene (15) and of substituted cyclopropanes to α -olefins (16) over the metathesis catalyst $\text{PhWCl}_3 \cdot \text{AlCl}_3$, and results from that work inferred that a mixture of $\text{W}=\text{CHC}_2\text{H}_5$ and $\text{W}=\text{CH}_2$ species would be generated from ethylcyclopropane. When a mixture of ethylcyclopro-

pane with an α -olefin such as 1-pentene was exposed to the catalyst (68), a new internal olefin was formed selectively (3-heptene in this case). This result was interpreted as indicating a predominantly nucleophilic character of the metathesis carbene. As with the tantalum carbene reaction, steric considerations, which would have favored a different course of reaction, were apparently not determining factors. These results were consistent with the influence of polarization according to Eq. (29).



Additional evidence for the contention that metathesis carbenes are nucleophilic was offered by Gassman in an interesting series of trapping experiments utilizing Michael acceptors as carbene traps (15, 17). Thus, an ethylidene carbene generated from 2-butene was trapped by ethyl acrylate to yield the expected ethylcyclopropyl ester, although yields were quite low.

In marked contrast to the results of Gassman and Schrock, major differences were noted by Casey and co-workers in a series of studies utilizing phenylcarbene-substituted $\text{W}(0)$ complexes in reactions with olefins. The ^1H NMR spectra of new phenylcarbene tungsten and iron (69) complexes indicate a substantial positive charge residing on the carbene carbon, and as expected, these complexes readily form ylides on reaction with phosphines:



Some notable reversals in the order of olefin reactivities were observed in contrast to the tantalum carbenes. Further, in comparing the reactivities of $(\text{CO})_5\text{W}=\text{CPh}_2$ and $(\text{CO})_5\text{W}=\text{CHPh}$, Casey (70) noted additional striking contrasts: The monophenyl carbene complex reacted rapidly at

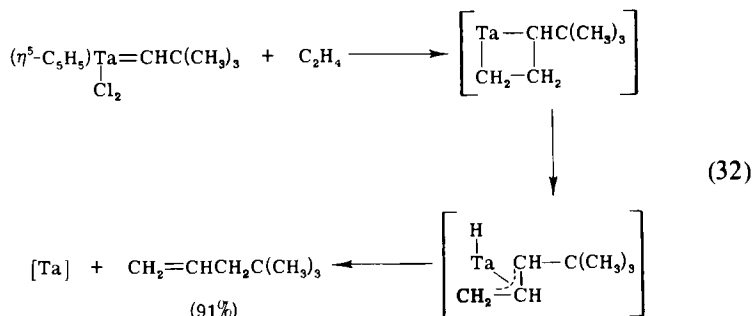
-78°C with olefins to yield cyclopropanes exclusively rather than metathesis products, and evidence favored a concerted insertion of the carbene into the double bond, either via direct reaction or via a metallocyclobutane. On the other hand, the diphenylcarbene complex required elevated temperatures to react (50° – 100°C) and afforded mainly metathesis-related olefins, along with minor amounts of cyclopropanes. In addition, $(\text{CO})_5\text{W}=\text{CHPh}$ reacted with isobutylene 350 times as fast as with propylene, in accordance with a strictly nucleophilic attack on the olefin, whereas the relative order of reactivity of $(\text{CO})_5\text{W}=\text{CPh}_2$ with olefins was 1-pentene $>$ isobutylene $>$ 2-butene \gg 2-methyl-2-hexene. This latter order of reactivity is not completely in accord with either nucleophilic or electrophilic attack on the olefin, indicating the possibility of more than one reaction pathway. The reactions of mono- and diphenylcarbene-tungsten pentacarbonyls with olefins are further complicated by the following facts: (a) The diphenylcarbene moiety is much weaker as a nucleophile and simultaneously is much more sterically hindered than the monophenylcarbene; (b) dissociation of the CO ligand occurs under the reaction conditions for the diphenylcarbene and indeed seems essential, thus providing sites for olefin precomplexation which is precluded in the low-temperature reactions of the monophenylcarbene complex; and (c) the relative proportions of olefin and cyclopropane products in reactions of the diphenylcarbene complex [processes **b** and **d** in Eq. (26)] vary according to the substrate olefin. The chemistry of this complex reflects competing influences of several factors which are not well accounted for.

The reactions reported by Casey (14) for a third carbene complex, $(\text{CO})_5\text{W}=\text{C}(\text{CH}_3)\text{Ph}$, are not pertinent to the present topic because extremely rapid β -H transfer to tungsten at -78°C initiates a sequence of reactions unique to this particular complex. This type of H transfer is atypical of conventional metatheses.

The above results appear to indicate that the chemistry of zero-valent model carbene systems does not adequately reflect the behavior of conventional active metathesis catalysts having intermediate oxidation states and bearing ionic ligands.

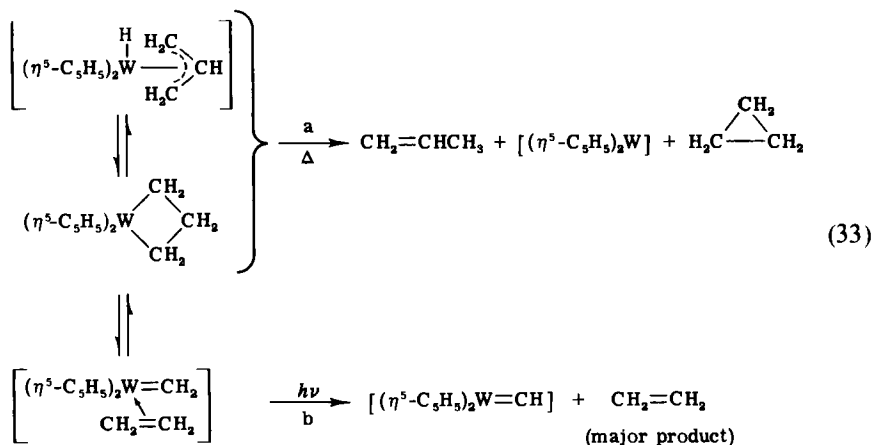
The course of decomposition of confirmed or presumed metallocyclobutane intermediates is important, but most results reported deal with stoichiometric rather than catalytic processes. Retention of the 3-carbon skeleton via pathways **d** or **f** in Eq. (26) occurs much more frequently than does cleavage to metathesis-related products. For example, thermolysis of phenyl-substituted platinocyclobutanes yields propenylbenzenes and phenyl-cyclopropane, but no styrene or ethylene (71). Similarly, the decomposition of tantalum carbene adducts (8) with olefins

yields substituted propylenes predominantly via pathways **f-h** of Eq. (26):



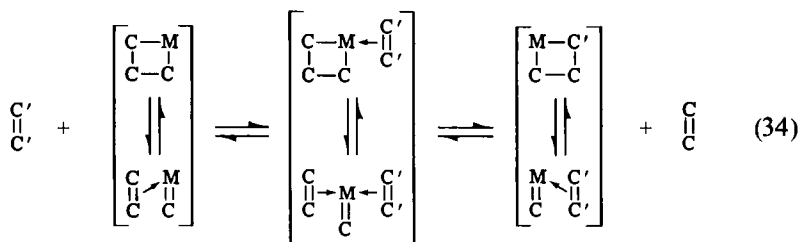
Other bimolecular reactions of metal-carbenes with olefins to yield cyclopropanes are also known.

In a more closely related example, $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_2)_3$ also leaves the 3-carbon skeleton intact (49), as shown in Eq. (33).



Reaction pathways apparently analogous to **d** and **f** of Eq. (26) yield a mixture of propylene and cyclopropane. Only when photochemical activation was employed were the major products olefins derived from metathesis-decomposition of the metallocycle. The failure to form metathesis olefins under moderate conditions is significant. It may be that either unimolecular dissociation of the olefin from the complex (in the absence of excess olefin to restabilize the carbene) is energetically unfavored, or the metallocyclobutane structure in the equilibrium given by steps **a** and **b** in Eq. (26) is highly stabilized and favored. These results

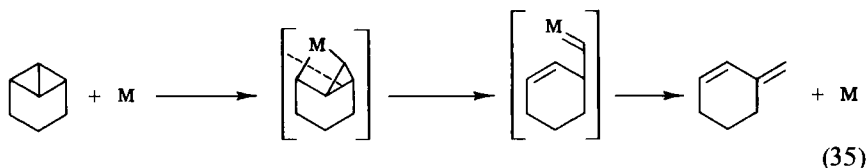
also suggest that nucleophilic displacement of a coordinated olefin, either from the metallocycle or from the olefin-carbene complex, may require precomplexation of a second olefin molecule:



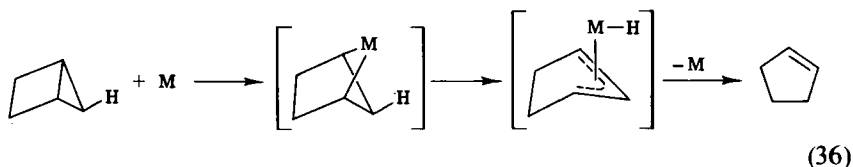
The importance of olefin precoordination is highlighted in this scheme.

Metallocyclobutanes from cyclopropanes have been frequently invoked in transition metal-catalyzed rearrangements of strained ring hydrocarbons, and this body of chemistry is quite rich and diverse, as evidenced in the excellent review by Bishop (72). Because of this diversity, the significance of isolated observations should not be overstated; nevertheless, certain reactions outlined by Bishop are closely related to the carbene retroadditions reported by Gassman and co-workers using metathesis catalysts.

Bicyclobutane derivatives react with rhodium complexes to give products which convincingly implicate metallocycles and metal-carbene species (72).

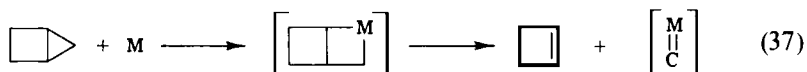


On the other hand, bicyclopentane rearranges to cyclopentene. In this case, a β -hydrogen shift occurs analogous to pathway *f* in Eq. (26) above:



A quite different result was reported by Gassman and Johnson (17) recently when the $\text{PhWCl}_3 \cdot \text{AlCl}_3$ metathesis catalyst was employed. Bi-

cyclopentane formally eliminated methylene to give a 70% yield of cyclobutene. A metallocycle different from that in Eq. (36) is implicated:



This process is quite unexpected for another reason. The cyclobutene ring is highly strained, making this monomer one of the most easily polymerized of all the cycloolefins. Thus, the variety of catalysts effective for cyclobutene polymerization is much broader than that effective for metathesis of low-strained cycloolefins and acyclic olefins (73). Therefore, the recovery of monomeric cyclobutene rather than its respective polymer is remarkable and indicates the lack of substantial metathesis activity in the above retrocarbenation system.

In considering catalyzed olefin-cyclopropane interconversions, an important question arises concerning thermodynamic control and the tendency (or lack thereof) to attain a state of equilibrium for the system. Mango (74) has recently estimated the expected relative amounts of ethylene and cyclopropane for various reaction conditions and concluded that the reported results were contrary to thermodynamic expectation. In particular, the "vigorous" formation of ethylene from cyclopropane (16) at -78°C was stated to be especially unfavored. On the basis of various reported observations and considerations, Mango concluded that a reaction scheme such as that in Eq. (26) above (assuming no influence of catalyst) was not appropriate, because the proper relative amounts of cyclopropanes and olefins just do not occur. However, it can be argued that the role of the catalyst *is* in fact an important element in the equilibration scheme, for the proposed metal-carbene and $[\text{M}^*]$ species in Eq. (26) are neither equivalent nor freely interconverted under normal reaction conditions. Consequently, all the reaction pathways are not simultaneously accessible with ease, as seen in the published literature, and the expected equilibria do not really have an opportunity for attainment. In such a case, absence of thermodynamic control should not a priori deny the validity of Eq. (26).

At this early stage of comprehension of the interrelation between metathesis and cyclopropanation, many questions remain. Why is the formation of cyclopropanes such a rare occurrence with typical metathesis catalysts, yet favored with some zero-valent carbene complexes? What is the role of prior complexation of the olefin with the metal in determining the reaction course for metal-carbene species? How are typical metathesis carbenes polarized, and how does this polarization influence selectivity of metathesis reactions (e.g., regenerative metathesis of α -

olefins) or the tendency for cyclopropanation? The occurrence of cyclopropanation appears to correlate best with the presence of nucleophilicity in the carbene carbon, except in reactions with Michael acceptors. Why is β -hydrogen transfer to metal not a more common occurrence, as it was demonstrated (14) to proceed at ease with $(\text{CO})_5\text{W}=\text{C}(\text{CH}_3)\text{Ph}$ at -78°C ? What accounts for the apparent lack of thermodynamic control in cyclopropane-olefin interconversion? These and other problems relating to the central scheme continue to be a challenge.

IV

STEREOCHEMICAL ASPECTS OF THE OLEFIN METATHESIS REACTION

One of the most intriguing features of olefin metathesis, and an aspect which continues to receive increasing attention, is the stereochemistry of the reaction. Rationalizations of stereochemical peculiarities have undergone a metamorphosis which parallels advances of mechanistic theories from the pairwise scrambling schemes to the now-popular carbene-to-metallocycle scheme. As yet there exists no unified stereochemical model which can adequately account for all the observed results.

A. Assumptions and Definitions

Substantial data exist in the literature to demonstrate that the metathesis reaction itself is a means for *cis* \rightleftharpoons *trans* interconversions. For the purpose of this discussion, it is assumed that metathesis is the *only* pathway for *cis* \rightleftharpoons *trans* isomerization.

Stereospecificity as applied to olefin metathesis may be considered in two ways: (a) How does the *cis*/*trans* isomer ratio of a product olefin compare with its equilibrium ratio, or (b) how does this *cis*/*trans* value differ from 1.0, which is the statistically expected value in terms of probabilities. In the present discussion, the latter definition applies.

With but few notable exceptions (75-77), an inherent characteristic of the metathesis of acyclic olefins with both homogeneous and heterogeneous catalysts is the tendency for attainment of thermodynamic equilibrium in the composition of *cis* and *trans* isomers in reactions carried to high conversion. Therefore, any inherent stereospecificity can only be evaluated by extrapolating compositional data to zero percent reaction.

Any acceptable account of the steric course of olefin metathesis must also take into consideration the following experimentally observed facts:

(a) The structure of the reacting olefin influences initial isomer distributions in product olefins.

(b) The *cis*/*trans* ratios of initially formed olefins depend not only on the precursor olefin structure but on the specific catalyst system.

(c) Some catalysts which exhibit good activity for *cis*-specific polymerization of certain cycloolefins display very poor activity in metathesizing acyclic olefins (78-80).

Various attempts to rationalize stereochemical results are inadequate in accounting for specific catalyst effects. The existing schemes rely primarily on steric interactions attributed primarily to alkyl substituents residing on the intermediate metallocycle ring.

B. Acyclic Olefins

The preponderance of stereochemical data in the literature has been obtained from studies using 2-pentene, which now appears to have been a rather poor substrate for emphasizing steric aspects of the reaction. Recent experiments utilizing 4-methyl-2-pentene (76) have given much clearer indications of steric control in metathesis reactions (*vide infra*).

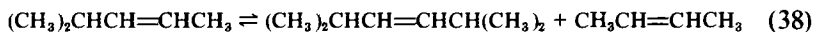
Soluble metathesis catalysts yield *trans* products in reactions with *trans*-2-pentene, but generally are not very stereospecific with *cis*-2-pentene. In the latter case, the initially formed butenes and hexenes are typically about 60 and 50% *cis*, respectively. Basset noted (19) that widely diverse catalyst systems behaved similarly, and so it was suggested that the ligand composition about the transition metal was not a significant factor in the steric course of these reactions. Subsequently, various schemes to portray the stereochemistry have been proposed which deal *only* with interactions involving alkyl substituents on the reacting olefin or on the presumed metallocyclobutane intermediate.

Occasionally, however, stereospecific results are encountered in the literature which clearly implicate ligands about the transition metal in steric control. For example, when a typical catalyst system based on WCl_6 was modified by the addition of triphenylphosphine, Dall'Asta found (77) that the reaction of *cis*-2-pentene led very selectively to the formation of *trans*-olefinic products. On the other hand, Katz demonstrated (75) that when $(\text{CO})_5\text{W}=\text{C}(\text{Ph})_2$ was used, *cis*-2-pentene afforded butenes and hexenes having about 95% *cis* structure, and notably that this specificity persisted even for reactions carried to near-equilibrium.

A pronounced *cis* specificity when using *cis*-2-pentene was also noted earlier by Hughes (78) with a soluble molybdenum catalyst. As a result, any attempt to rationalize steric factors which ignores specific catalyst effects is vulnerable to error.

Fortunately, steric control arising from interactions of alkyl moieties derived from reacting olefins can be enhanced and observed by selection of appropriate reactants. This effect was demonstrated in the work of Lawrence and Ofstead (76), who studied the metathesis of 4-methyl-2-pentene induced by a $\text{WCl}_6 \cdot \text{Et}_2\text{O} \cdot \text{Bu}_4\text{Sn}$ catalyst. This catalyst is not particularly unique, for the steric course of the metathesis of *cis*-2-pentene with this system was found to be essentially equivalent to that previously observed (18) with a conventional catalyst employing an organoaluminum cocatalyst.

4-Methyl-2-pentene afforded the expected products, 2-butene and 2,5-dimethyl-3-hexene, a highly hindered olefin. (The equilibrium *cis* content of an equilibrated mixture of 2,5-dimethyl-3-hexene isomers was independently established to be 7% *cis*.)



Compositions of metathesis reaction mixtures obtained over a range of conversions starting with *cis*- and *trans*-4-methyl-2-pentene are shown in Figs. 1 and 2, respectively. Certain important differences are evident in comparisons with the course of reactions of 2-pentene isomers (18).

The foremost observation was the highly specific formation of 99%

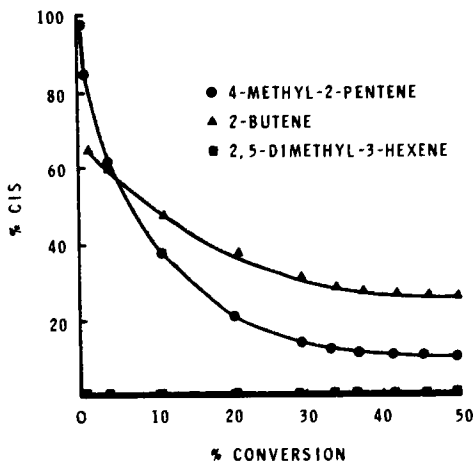


FIG. 1. The metathesis of *cis*-4-methyl-2-pentene. Effect of conversion on products structure (76).

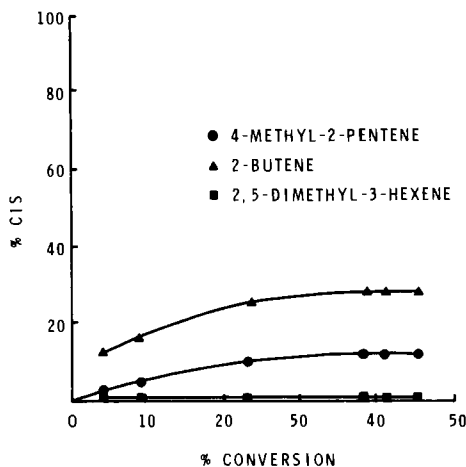


FIG. 2. The metathesis of *trans*-4-methyl-2-pentene. Effect of conversion on products structure (76).

trans-2,5-dimethyl-3-hexene throughout the course of the reaction, regardless of the structure of the starting olefin. The greater steric requirement of the isopropyl group in comparison with an ethyl or methyl resulted in a marked change in the course of the reaction.

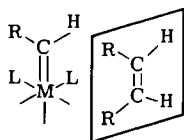
A second observation was the fact that isomerization of the starting asymmetric olefin was much faster than the formation of new symmetric olefins. In fact, 40% of the initial *cis* olefin (Fig. 1) had isomerized to *trans* after only 4% conversion to new olefins. This result formally parallels the highly selective regenerative metathesis of α -olefins (60, 61), except that steric factors now prevail, because electronic effects should be minimal. Finally, the composition of the initially formed butene from *cis*-4-methyl-2-pentene was essentially identical to that obtained when *cis*-2-pentene was used (18). When *trans*-4-methyl-2-pentene was metathesized (Fig. 2), the composition of the initially formed butenes indicated a rather high *trans* specificity.

The above results clearly demonstrate influences of the steric requirements of various alkyl groups on the course of the reaction, and these effects must be reconciled in any mechanistic scheme.

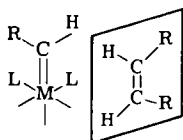
From a consideration of data provided in studies limited to the metathesis of 2-pentene, several views of the stereochemistry have been recently advanced. For the most part, they deal only with steric influences caused by alkyl groups coming from the reacting olefin.

Basset and co-workers have formulated a reaction model (81, 82) wherein the structure of the intermediate metallocycle is predetermined

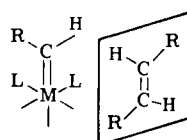
by steric factors governing the orientation of the olefin approaching the metal-carbene bond. Their model presumes only four substituents about the transition metal: the carbene, the coordinated olefin, and two additional ligands. The alkyl group on the carbene is preferentially oriented away from one of the ligands, and the coordinated olefin then assumes an orientation which provides for a minimum of alkyl-alkyl and alkyl-ligand repulsions. Representative configurations for reactions of *cis*-olefins are given in structures A and B, and the preferred configuration for reaction of a *trans*-olefin is given by C.



(A)



(B)



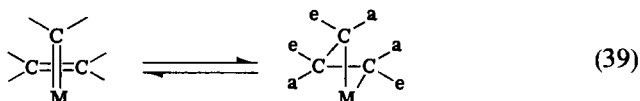
(C)

Structure A leads to *cis* products, structure B to *trans* products. Neither structure was favored in Basset's scheme, and this was consistent with typically observed nonstereospecific metathesis of *cis*-2-pentene. Structure C favors formation of *trans* products, as is widely observed.

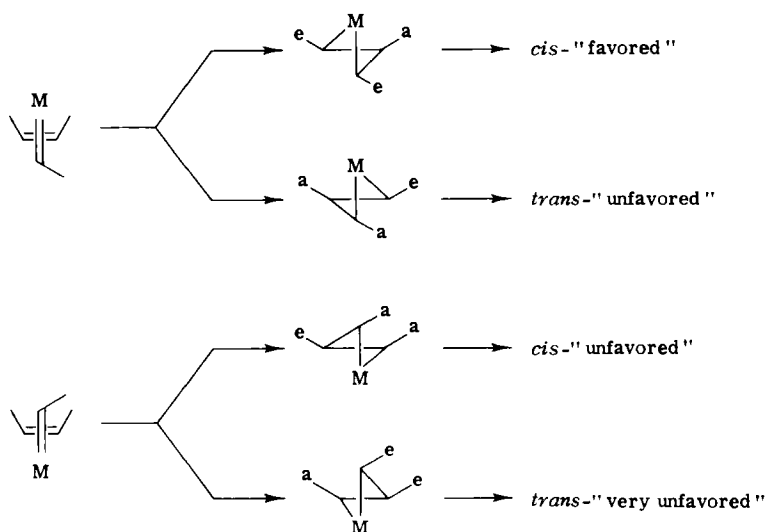
This model represents an effort to deal with ligand effects, but it is difficult to believe that the wide variety of catalysts studied can universally be as coordinatively unsaturated as this model requires. In fact, even pentacoordinate forms of tungsten (e.g., $W(CO)_5$) are generally held to be much less stable than hexacoordinate species. Their scheme would also seem to predict the highly selective the formation of *cis*-butene from *cis*-4-methyl-2-pentene, whereas the observed stereospecificity is virtually the same as that obtained with *cis*-2-pentene (18).

An alternative approach has been formulated by Katz and co-workers (28). They consider the latent *cis* specificity in reactions of *cis*-olefins with metathesis catalysts to be quite high, based on their results with a catalyst having very low Lewis acidity. They further propose that the frequently observed lack of stereospecificity is mainly the consequence of cationic processes inherent in the metathesis step which mask stereospecificity.

Katz describes the reaction as a rearrangement which is preceded by the approach of an olefin oriented perpendicular to the metal-carbene. Precomplexation of the olefin was not specified.



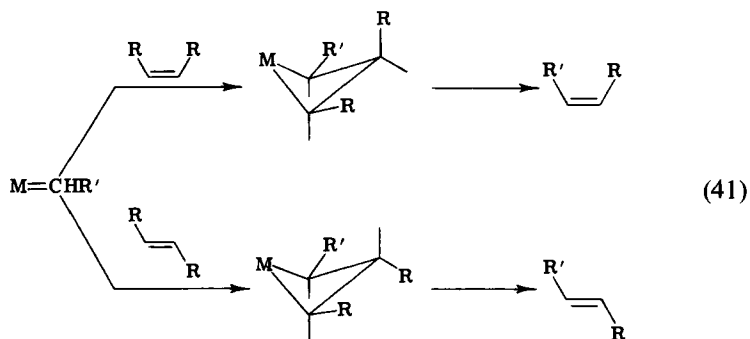
In this scheme, a highly puckered metallocycle was envisioned, possessing pseudoaxial and equatorial substituents, and reaction pathways were said to be favored which minimized the following effects: (a) 1,3-diaxial interactions of substituents on the two α -carbons; (b) axial substituent interactions with juxtaposed ring carbons; and (c) 1,2-diequatorial interactions. This scheme predicts relatively nonstereospecific metathesis of *trans*-olefins but highly stereospecific metathesis of *cis*-olefins. For example, the following pathways for reactions of *cis*-olefins were proposed:



This scheme now appears to be of very limited predictive value, because the results described previously with *cis*-4-methyl-2-pentene, which selectively gave pure *trans*-C₈ as one of the products (76), would be entirely unexpected. Furthermore, if the commonly observed lack of stereospecificity in reactions of *cis*-2-pentene were to be attributed to an ionic process involving the metallocyclobutane, one would not expect uniformly similar steric results with diverse catalysts such as those summed up by Basset (81), as varying degrees of cationic isomerization would have been expected with these diverse catalysts.

Casey and co-workers visualized the stereochemistry of 2-pentene metathesis in terms of the relative stabilities of the various substituted metallocycle derivatives (14). As in Katz's scheme, a puckered ring was assumed, but Casey emphasized only that reaction pathways were favored which provided conformations possessing the fewest axial substit-

uents on the α -carbons in the ring. Retention of configuration was provided by this scheme.

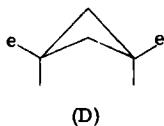


Unfortunately, this scheme does not anticipate the nonspecific formation of 50% *trans*-3-hexene from *cis*-2-pentene, nor the course of reaction for *cis*-4-methyl-2-pentene mentioned earlier.

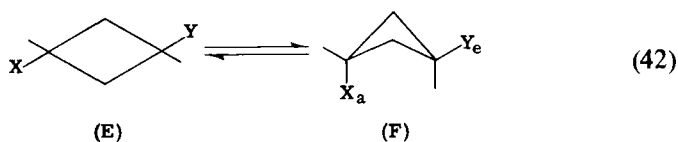
Information regarding conformational and configurational stabilities in substituted metallocyclobutanes would be most valuable, but very little is known. An X-ray crystallographic study of $(\text{CH}_2)_3\text{PtPy}_2\text{Cl}_2$ indicated a slightly folded ring having an angle of about 12° between the two planes, but experimental difficulties with this measurement made the value barely statistically significant (83).

By analogy with cyclobutane chemistry, some guidelines can be suggested. Four factors are important (84):

(a) The degree of puckering in cyclobutanes varies markedly (0° – 35°) with the type of substitution. For *cis*-1,3-disubstitution, puckering is enhanced, and provides for favored diequatorial orientation of substituents,



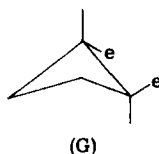
where *trans*-1,3-disubstitution often results in a planar conformation (E) of the ring in order to minimize axial interactions (F):



Therefore, one cannot presume a fixed amount of puckering to occur in various substituted metallocyclobutanes.

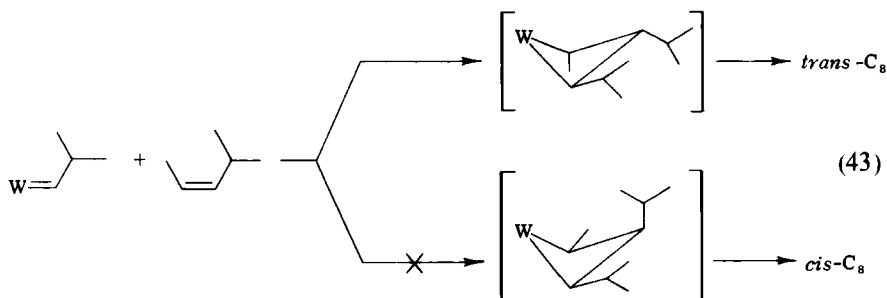
(b) When bulky groups are substituted in 1,3-positions on cyclobutane, the *cis* isomer is favored somewhat over the *trans* isomer. An equilibrated mixture of 3-*tert*-butylcyclobutanecarboxylic acid esters contained a 2/1 ratio for the *cis*/*trans* isomers.

(c) For 1,2-disubstituted cyclobutanes, *trans* substitution is highly favored over *cis* substitution. In a puckered ring, these substituents would assume a pseudoequatorial orientation, but apparently *e-e* repulsions are minor, in contrast to the proposal of Katz that such repulsions are substantial.



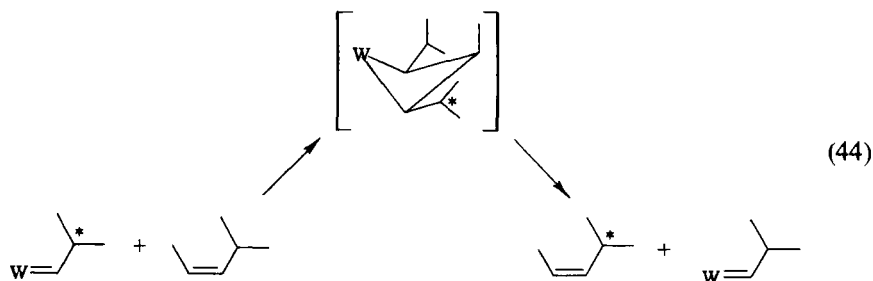
(d) When isopropyl or *tert*-butyl substituents are present, these bulky groups now command an exclusively equatorial orientation. No such steric demand exists for the smaller methyl or ethyl groups.

With these guidelines, the results from the metathesis of 4-methyl-2-pentene now appear to be reasonably accountable for. Most importantly, the lack of formation of *cis*-2,5-dimethyl-3-hexene indicates that *cis*-1,2-diisopropyl-substitution on the ring is highly unfavored, and *trans*-1,2-substitution leading to adjacent equatorial substituents is acceptable:

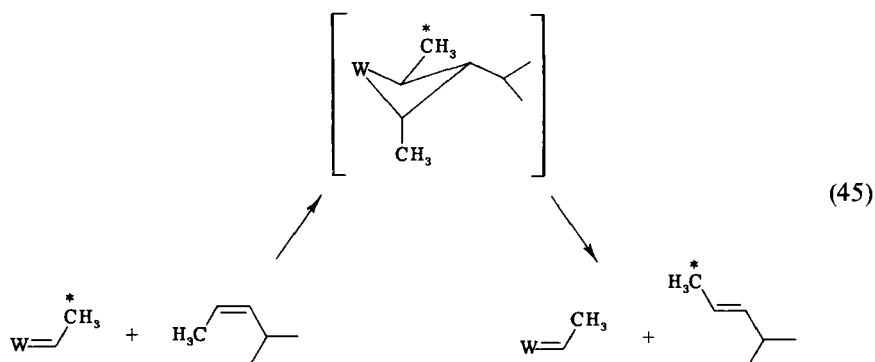


The rapid isomerization of *cis*-4-methyl-2-pentene relative to productive metathesis suggests further information regarding the isomerization process. If regenerative metathesis proceeded selectively via an isopropyl carbene, and assuming that the isopropyl groups maintained equatorial

orientations, then regenerative metathesis would proceed entirely with retention of configuration:



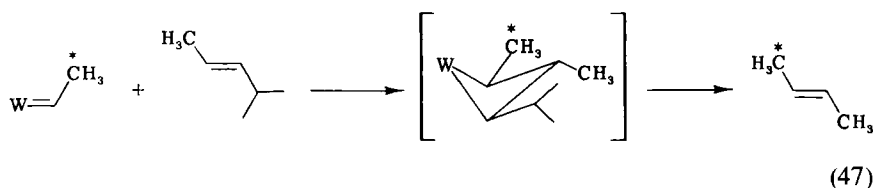
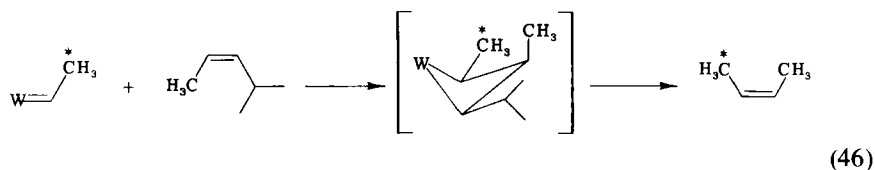
Alternatively, if regenerative metathesis involved preferentially a methyl-substituted carbene, the preferred metallocyclobutane would favor isomerization of the starting olefin.



Equation (45) appears more consistent with the experimental results of Lawrence than Eq. (44). This scheme also implies some influence of the tungsten ligands in directing the bulky group away from the metal.

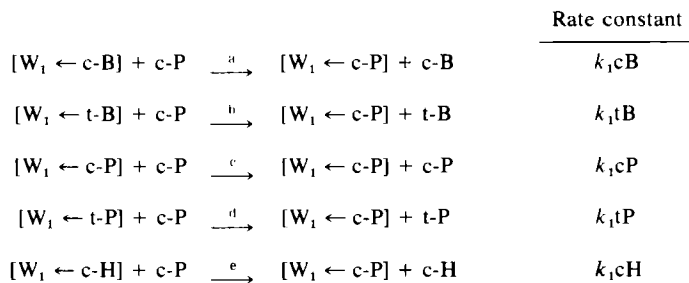
The moderate specificity for forming *cis*-2-butene initially (see Fig. 1) is again consistent with equatorial orientation of isopropyl; the rather low *cis* specificity indicates only a moderate preference for equatorial orientation of the α -methyl, probably because of the offsetting weak repulsions caused by *cis*-1,2-dimethyl-substitution. This effect is absent in the metathesis of *trans*-4-methyl-2-pentene, and *trans* specificity for

initially formed 2-butene (Fig. 2) is considerably higher:



It would be tempting to apply the same rationale to the metathesis of 2-pentene isomers, but clearly, the steric requirements of methyl and ethyl are much less than that of isopropyl, and trade-offs involving *cis*-1,2-disubstitution vs. axial orientation are not clear; neither is the important role of catalyst ligand influence.

There is a basic deficiency in all the aforementioned efforts to interpret the steric course of olefin metathesis. By entirely ignoring the existence of the exchange step, i.e., the process by which an incoming reactant olefin replaces a product olefin, they unavoidably assume a priori that all the possible exchanges have a common rate constant, or else are much faster than the actual transalkylidenation step. For *cis*-2-pentene alone there exist 12 different exchange processes where it replaces *cis*- and *trans*-2-butene, 2-pentene and 3-hexene from $[\text{MeCH}=\text{W}]$ and $[\text{EtCH}=\text{W}]$ metallocarbenes. Let $[\text{MeCH}=\text{W}] = \text{W}_1$ and $[\text{EtCH}=\text{W}] = \text{W}_2$; c-B, c-P, c-H and t-B, t-P, t-H are the participating *cis* and *trans* isomers; $[\text{W}_1 \leftarrow \text{c-B}]$ denotes a *cis*-2-butene complexed to a $[\text{MeCH}=\text{W}]$, etc. Then the following exchange sequences are to be considered:



		Rate constant
$[W_1 \leftarrow t-H] + c-P \xrightarrow{f}$	$[W_1 \leftarrow c-P] + t-H$	k_1tH
$[W_2 \leftarrow c-B] + c-P \xrightarrow{g}$	$[W_2 \leftarrow c-P] + c-B$	k_2cB
$[W_2 \leftarrow t-B] + c-P \xrightarrow{h}$	$[W_2 \leftarrow c-P] + t-B$	k_2tB
$[W_2 \leftarrow c-P] + c-P \xrightarrow{i}$	$[W_2 \leftarrow c-P] + c-P$	k_2cP
$[W_2 \leftarrow t-P] + c-P \xrightarrow{j}$	$[W_2 \leftarrow c-P] + t-P$	k_2tP
$[W_2 \leftarrow c-H] + c-P \xrightarrow{k}$	$[W_2 \leftarrow c-P] + c-H$	k_2cH
$[W_2 \leftarrow t-H] + c-P \xrightarrow{l}$	$[W_2 \leftarrow c-P] + t-H$	k_2tH

Hence, the observed concentration of a given olefin at early stages of reaction depends both on its rate of formation from the respective metallocyclobutane and on its tendency to be displaced by an incoming *cis*-2-pentene. Thus, an argument could be advanced that the observed moderate stereoselectivity reflects minor variations in the respective rate constants of exchange steps, and that the steric constraints in forming the metallocyclobutane are not kinetically significant in product formation. To resolve this issue, one needs to study metathesizing systems that retain steric selectivity *throughout the reaction*, i.e., for which the redistribution of alkylidenes reaches equilibrium but maintains a large degree of geometric purity. The reaction of *cis*-4-methyl-2-pentene to give >99% *trans*-2,5-dimethyl-3-hexene throughout the entire course of reaction seems to clearly indicate that transition state stabilities are being observed, and not simply rate of displacement of product olefins.

C. Cycloolefins

Whereas marked stereospecificity in the metathesis of acyclic olefins is rare, in cycloolefins it is not uncommon. High-*cis* polypentenamer can be prepared by $MoCl_5/R_3Al$ as well as by WF_6/R_2AlCl and $WCl_6/R_3Al/(BzO)_2$ catalyst systems (20–22). High-*trans* polypentenamer is obtained by a variety of catalytic systems. Figure 3 illustrates the microstructure of polypentenamer vs. conversion for several tungsten-based catalyst systems. Notice that the systems do vary in terms of yielding different initial and final microstructures, and the $WF_6/C_2H_5AlCl_2$ ($Al/W = 1.0$) never reaches the 84%-*trans* equilibrium polypentenamer structure.

The diverse steric course of the metathesis of cyclic vs. acyclic olefins poses a dilemma. It stands to reason that once a cycloolefin monomer

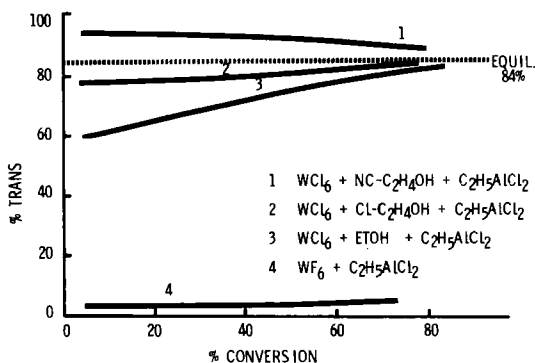
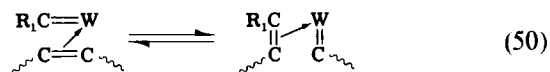
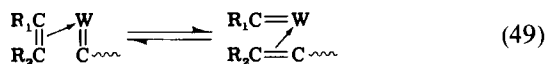
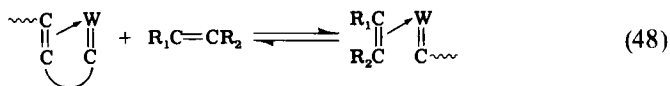


FIG. 3. Effect of catalyst and conversion on microstructure for cyclopentene polymerizations (79, 80).

undergoes a stereoselective metathesis, and thus is incorporated into a high molecular weight chain, its vinylene moiety is no longer cyclic but linear. Therefore, further metathetic steps involving polymeric vinylene double bonds should degrade the initial stereospecificity and result in a mixture of cis and trans units; but this does not occur (*vide infra*). Using cyclopentene as an example, pentamer repeat units maintain their stereospecificity throughout the polymerization when cis-specific catalysts are used.

In an attempt to further understand these observations, cis-directing catalysts for cyclopentene were examined in terms of their capability to metathesize acyclic olefins.

Acyclic olefins act as chain scission agents in cycloolefin polymerization; hence, they are employed as molecular weight regulators. Equations (48)–(50) illustrate the sequence by which chain scission is achieved:



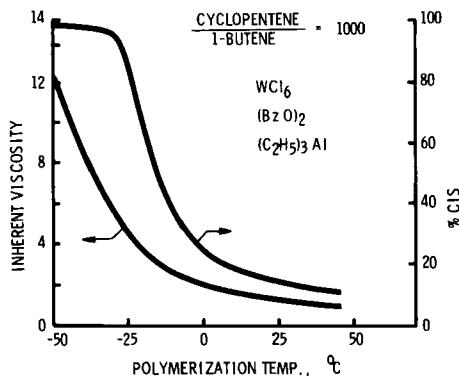


FIG. 4. Effect of temperature on microstructure and inherent viscosity for cyclopentene polymerizations (22).

Note that the alkylidene moieties of the acyclic olefin act as capping groups for the polymeric chains. Theoretically, by adjusting the ratio of cyclic to acyclic olefins one could vary the molecular weights of polyalkenamers at will from liquid oligomers to macromolecules having molecular weights of 10^6 and higher.

The stereospecific catalysts capable of yielding high-cis polypentenamers were found to be generally ineffective in metathesizing acyclic olefins.

Figure 4 presents Minchak's results (22), where a $WCl_6/(BzO)_2/(C_2H_5)_3Al$ catalyst exhibited high cis selectivity at temperatures below $-25^\circ C$, and the effect of 1-butene as a molecular weight regulator was nil. With increase in temperature the cis selectivity was lost, and a simultaneous drastic drop in molecular weight was experienced, indicat-

TABLE II
POLYMERIZATION OF CYCLOPENTENE IN THE
PRESENCE OF 2-PENTENE BY $WF_6/C_2H_5AlCl_2$
CATALYST^a

$C_2H_5AlCl_2/WF_6$	Polymer structure (% cis)	\bar{M}_v ^b
1	94	1,500,000
5	38	110,000

^a If cyclopentene and 2-pentene were equally reactive, expect $\bar{M}_v = 70,000$.

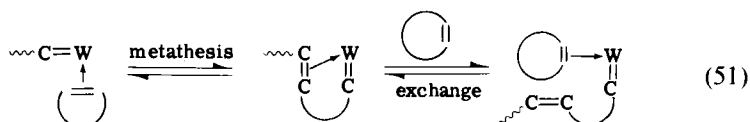
^b $[\eta]_{tol} = 5.21 \times 10^{-4} \bar{M}_v^{0.69}$.

ing that the participation of acyclic olefins occurs when the catalyst ceases its *cis* selectivity.

A comparative experiment, using $\text{WF}_6/\text{AlCl}_3$ catalyst at $\text{Al/W} = 1$ and $\text{Al/W} = 5$, was carried out at room temperature on a cyclopentene/2-pentene mixture (molar ratio of 500/1). The results are summarized in Table II. Notice that the observed molecular weights approach the expected values as the *cis* selectivity of the catalyst is reduced.

Table III presents additional cyclopentene polymerization data with 1-pentene as a regulator at 0°C throughout a wide range of conversion. As long as the *cis* selectivity is maintained, the regulator remains inactive and does not participate in the scrambling process.

It is proposed that nonselective cycloolefin metathesis proceeds by a "two-ligand" sequence:



In contrast, *cis*-selective metathesis proceeds by a "three-ligand" sequence:

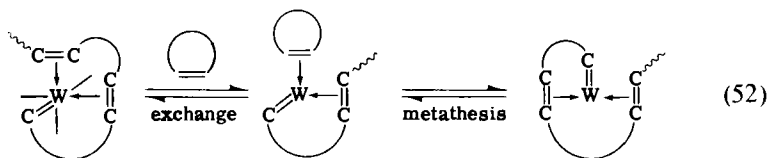


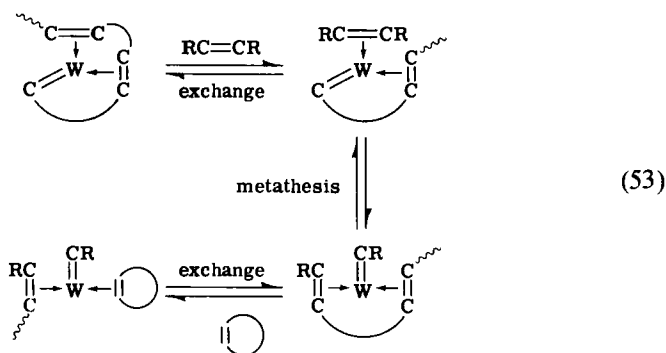
TABLE III
CYCLOPENTENE POLYMERIZATION, $\text{WF}_6 + \text{EtAlCl}_2$,
CYCLOPENTENE/1-PENTENE = 40

Time (min)	Conv. (%)	cis (%)	Inh. visc., dl/g	$\sim \bar{M}_v$ ^a
5	26.2	97.5	6.0	770,000
10	42.3	96.9	5.2	620,000
20	54.3	97.1	5.4	660,000
40	64.4	—	4.6	520,000
60	65.8	95.5	5.2	620,000
80	67.1	—	4.8	560,000
100 ^b	67.6	95.9	5.0	590,000

^a For CP/1-P = 40, predict $\bar{M}_v \sim 5440$ (inh. visc. ~ 0.20).

^b Gas-liquid chromatography indicated 99% of 1-pentene unreacted.

In the two-ligand sequence, the incoming monomer enters the coordination sphere of the metal and exchanges with the double bond of the ultimate monomeric unit. In the three-ligand sequence, the incoming monomer exchanges with the double bond of penultimate monomeric unit—thus maintaining a tridentate complexation after metathesis. The tridentate complex can be maintained as long as the exchanging double bond is a constituent of a cyclic structure. If an acyclic double bond exchanges at the penultimate position and metathesis ensues, a two-ligand sequence will result as depicted in Eq. (53). Because loss of chelation is necessary only when an acyclic olefin reacts, the net reaction of cycloolefin becomes much favored in this scheme relative to reaction of the acyclic olefin. An analogous phenomenon does not exist in the two-ligand scheme.



In summary, the interrelation of cis-selective catalysts and their lack of metathesis activity with acyclic olefins are rationalized by a speculative scheme that incorporates the concept of a tridentate "cagelike" complex as the active species of cis-directing catalysts.

V

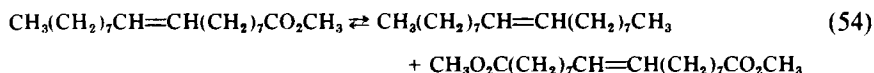
METATHESIS OF SUBSTRATES BEARING POLAR GROUPS

The metathesis of olefins substituted with polar functional groups is a relatively new venture. Until recently, most metathesis catalysts could not withstand the poisoning effects of electronegative atoms (such as O, N, and S). However, as a result of Boelhouwer's pioneering work (23), a newer generation of hardy catalysts has been discovered capable of tolerating a variety of functional groups. This art is now in a rapid state of development and its technological significance extends broadly into

applications relating to such areas as perfume chemistry, insect control, flame- and oil-resistant elastomers, and specialty plastics. An excellent all-inclusive review of this matter was presented by Streck (24). The object of this writing is to bring to the forefront questions regarding the apparent specificity of certain metathesis catalysts for polar-substituted olefins and the apparent lack of activity in others.

A. Functionalized Acyclic Olefins

Polar-substituted alkenes where the functionality is not attached to a strained ring are considerably more discriminating in their compatibility with metathesis catalysts and as a rule require relatively high catalyst charges. In the aliphatic series, unsaturated esters have received the most attention. Boelhouwer reported in 1972 the metathesis of the ester methyl oleate and its trans isomer, methyl elaidate, with a homogeneous catalyst based on a 1/1.4 molar combination of $\text{WCl}_6/(\text{CH}_3)_4\text{Sn}$ (23). At 70°C and an ester/W molar ratio of 33, near-thermodynamic equilibrium was attained, and 49 and 52% of the respective esters were converted to equal amounts of 9-octadecene and the dimethyl ester of 9-octadecene-1,18-dioic acid.

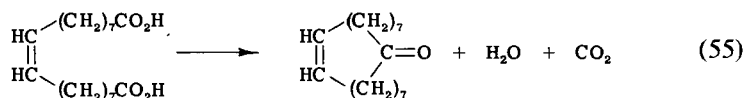


Cross-metathesis of methyl oleate with 3-hexene under similar conditions led, in addition to the above products [Eq. (54)], to 3-dodecene and the methyl ester of 9-dodecenoic acid.

Boelhouwer subsequently reported the successful metathesis of methyl esters of the polyunsaturated linoleic and linolenic acids using the $\text{WCl}_6/(\text{CH}_3)_4\text{Sn}$ catalyst (85). The metathesis reaction occurred both inter- and intramolecularly. Product distributions at equilibrium corresponded to a statistical scrambling of alkylidene and carboxyalkylidene moieties resulting in a 1/2/1 molar ratio of polyenes, monocarboxylic esters, and dicarboxylic esters. In addition, 1,4-cyclohexadiene and higher cyclopolyenes were detected. Conversions of methyl linolate and methyl linolenate were 84 and 95%, respectively. With the aid of gas chromatography-mass spectroscopy, Ast identified 5 linear olefins, 5 unsaturated monoesters, and 5 unsaturated diesters, in addition to 1,4-cyclohexadiene, which were produced by the $\text{WCl}_6/(\text{CH}_3)_4\text{Sn}$ -catalyzed metathesis of methyl linolate (86).

Triglycerides of unsaturated fatty acids, which are an abundant commodity, were shown to disproportionate with the $\text{WCl}_6/(\text{CH}_3)_4\text{Sn}$ catalyst

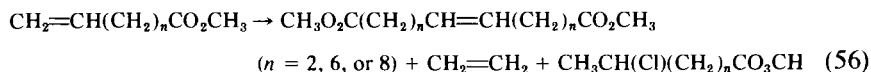
(87). These reactions, which are believed to occur predominantly intermolecularly, are capable of producing intermediates which hold some potential as precursors for important chemical products. For example, metathesis of olive oil, which consists chiefly of triglycerides of oleic acid, produces the glyceride of 9-octadecene-1,18-dioic acid from which can be obtained, after saponification, acidification, and low-temperature crystallization, the free acid, which can be transformed by intramolecular condensation to civetone.



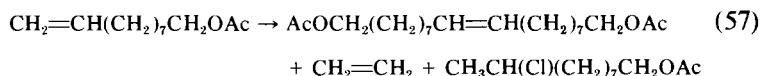
Intermolecular metathesis of linseed and soybean oils, which are triglycerides of linoleic and linolenic acids, offers an alternative method of upgrading these drying oils into stand oils by a net increase of their molecular weights.

Boelhouwer extensively screened numerous catalyst systems and found the $\text{WCl}_6/(\text{CH}_3)_4\text{Sn}$ combination to be unique for the metathesis of fatty acid esters (87). Seemingly related combinations, such as $\text{WCl}_6/(\text{C}_2\text{H}_5)_4\text{Sn}$, $\text{WCl}_6/(\text{C}_4\text{H}_9)_4\text{Sn}$, $\text{WCl}_6/(\text{Ph})_4\text{Sn}$, and $\text{MoCl}_5/(\text{Ph})_4\text{Sn}$ were surprisingly inactive in the homometathesis of fatty acid esters or in cross-metathesis reactions with common olefins. The unique activity of $(\text{CH}_3)_4\text{Sn}$ as a cocatalyst is unexplained at present; an understanding of this result would contribute to a better elucidation of the initiation process.

Boelhouwer's discovery (23) prompted a flurry of activity in this area. Baker applied the Boelhouwer catalyst to the metathesis of ω -olefinic esters (88). At an ester/W molar ratio of 20/1 (68°C), symmetrical olefinic diesters were formed in 34–36% yields with concomitant elimination of ethylene. In addition, Baker identified products recovered in 3–8% yield corresponding to addition of HCl across the terminal double bond.

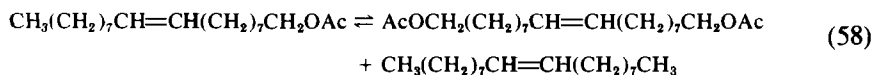


9-Decenyl acetate was also converted to a 32% yield of the corresponding diacetate and a 4% yield of HCl addition product.

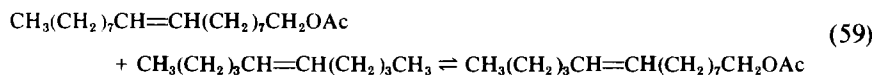


The cis/trans ratios in the corresponding products were found to reflect conditions of thermodynamic equilibrium.

Recently, additional catalyst systems which are effective for the metathesis of olefins bearing polar functional groups have been revealed. Nakamura and co-workers found that either WCl_6 or $(\text{C}_2\text{H}_5\text{O})_2\text{MoCl}_3$ in combination with triethylborane were capable of converting *cis*-9-octadecenyl acetate to 1,18-diacetoxy-9-octadecene and 9-octadecene at the rather high temperature of 178°C (89).



Subsequently, Nakamura reported that catalyst systems derived from WCl_6 , MoCl_5 , $\text{Mo}(\text{OC}_2\text{H}_5)_2\text{Cl}_3$, and $\text{W}(\text{CO})_6$ in combination with $(\text{CH}_3)_3\text{Al}_2\text{Cl}_3$ effected the disproportionation of a variety of fatty acid esters as well as the first reported metathesis reactions involving alkenyl nitriles, ketones, ethers, amides, and oxysilanes (90). A WCl_6 -based catalyst appeared to be the most effective. However, positional isomerization of the double bond leading to undesired metathesis side reactions decreased its selectivity. For example, with the WCl_6 catalyst and a molar ratio of ester/W/Al of 30/1/2, methyl oleate was converted at 28°C to 9-octadecene and 9-octadecene-1,18-dioic acid dimethyl ester in yields of 23 and 21%, respectively, according to Eq. (54). Cross-metathesis of oleyl acetate with 5-decene employing the same catalyst afforded a 26% yield of 9-tetradecenyl acetate together with traces of the homometathesis products.



Presumably, 7-tetradecene was also formed, but its presence was not reported. This reaction could be important as a means for the preparation of insect pheromones. This in itself presents a challenge; namely, discovering stereospecific catalysts which are capable of yielding the biologically active *cis* isomers.

As mentioned above, olefins substituted with *N,N*-dialkylamide, nitrile, *p*-methoxyphenyl, and ketone groups, as well as the compound trimethylallyloxysilane, were metathesized, albeit in low yields (2–10%), with an olefin/W/Al molar ratio of 15/1/3 using $\text{WCl}_6/(\text{CH}_3)_3\text{Al}_2\text{Cl}_3$ as catalyst (90). This catalyst failed to effect the disproportionation of unsaturated carboxylic acids, alcohols, primary amines, and unsubstituted carboxamides. It is interesting to note that catalysts such as $\text{WCl}_6/\text{C}_2\text{H}_5\text{OH}/\text{C}_2\text{H}_5\text{AlCl}_2$ and $\text{Re}_2\text{O}_7\text{--Al}_2\text{O}_3$ were completely inactive, and the more closely related catalysts $\text{WCl}_6/(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Cl}_3$, $\text{WCl}_6/(\text{C}_2\text{H}_5)_3\text{Al}$, and $\text{WCl}_6/(\text{CH}_3)_3\text{Al}_2\text{Cl}_3$, showed almost no catalytic activity with any of the polar substituted olefins (90).

Basset and co-workers (91) found that amino olefins such as allyl amine and the *N,N*-dimethyl derivative failed to undergo metathesis, but that unsaturated quaternary ammonium salts were active at 25°C with zero-valent tungsten and molybdenum catalysts when activated with molecular oxygen. Molar ratios of olefin/(mesitylene)W(CO)₃/C₂H₅AlCl₂/O₂ and olefin/Mo(NO)₂Cl₂[P(Ph)₃]/C₂H₅AlCl₂ were 20/1/24/80 and 20/1/24, respectively. Yields were in the 8–23% range.

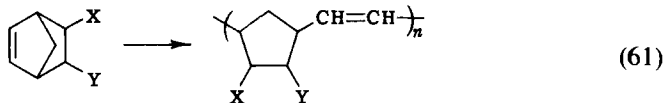


The first example of a heterogeneous catalyst able to metathesize olefinic esters was recently reported (92). The combination of Re₂O₇/(CH₃)₄Sn at an olefin/Re/Sn molar ratio of 219/6/1 converted methyl 4-pentenoate at 50°C in 51% conversion to ethylene and the corresponding dimethyl ester of 4-octene-1,8-dioic acid. This reaction exhibited a high degree of selectivity (>99%), and in the absence of (CH₃)₄Sn the rhenium catalyst was inactive (90).

B. Functionalized Cycloolefins

1. Norbornene Derivatives

The inhibitory effects of polar functional groups are not nearly as pronounced when the substituent is attached to a strained cycloalkene, where the release of ring strain provides a significant driving force for its metathesis. The norbornene ring system polymerizes easily by ring opening; thus, numerous functionalized polymers have been prepared by the sequence depicted in Eq. (61). Many of these polymers hold some potential for commercialization and hence the bulk of this work is reported in the patent literature.



The earliest reported ring-opening polymerizations of functionalized norbornenes were carried out in protic solvents (alcohol, water) using iridium, ruthenium, or osmium salts. Thus, norbornenes substituted with ester (93–95), hydroxy (95), chlorine (96), alkoxy (97), and imide (93) groups have been polymerized via metathesis using noble metal catalysts.

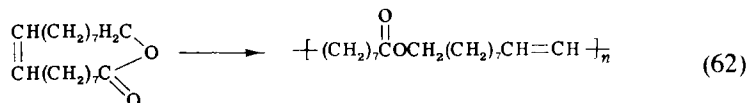
In some cases, some competing addition polymerization through the double bond was believed to have occurred (96).

Homogeneous catalysts based primarily on WCl_6 and organoaluminums have also been reported for norbornenes bearing ester (98-104), nitrile (102, 104-106), amide (104, 107), chlorine (108), imide (104, 109), anhydride (104), and pyridyl (104) functional groups. Monomer/W molar ratios generally in the range of 100-2000/1 were commonly employed. A significant advance here was the need for "catalyst modifiers," which substantially increased the catalyst activity. These modifiers are usually polar in nature and come from many structural classes. Among these are alcohols, peroxides, epoxides, acetals, $\text{Ti}(\text{OR})_4$, FeCl_3 , and $\text{Al}(\text{OR})_3$ (104).

Certain metal-carbene complexes such as $[(\text{CH}_3)_4\text{N}][(\text{CO})_5\text{WCOPh}]$ and $(\text{CO})_5\text{WC}(\text{OC}_2\text{H}_5)\text{Ph}$ in combination with PR_3 , sulfides, sulfoxides, quinones, or *N*-chlorosuccinimide, together with a TiCl_4 cocatalyst, were also effective catalysts, at monomer/W molar ratios of up to 5000/1 (104).

2. Miscellaneous Monomers

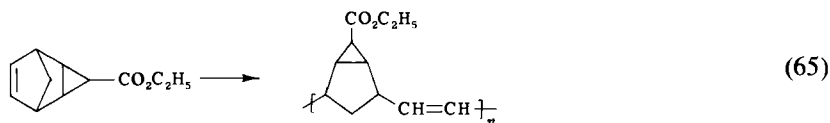
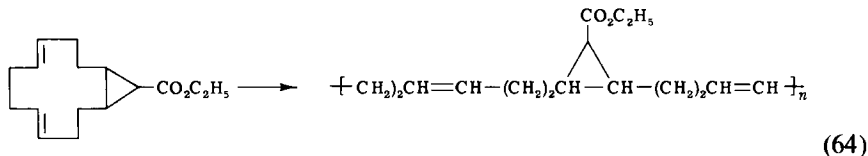
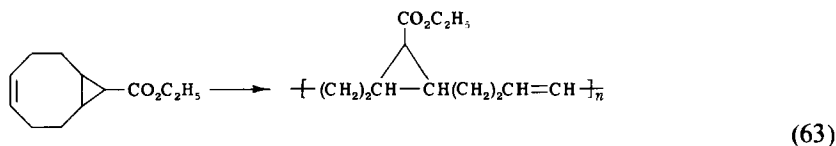
A naturally occurring lactone, ambrettolide, was polymerized (110) employing the $\text{WCl}_6/(\text{CH}_3)_4\text{Sn}$ catalyst in a molar ratio of monomer/W/Sn of 50/1/5, affording a high molecular weight unsaturated polyester.



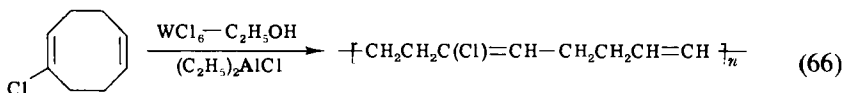
Conversions of about 80% were obtained within a few minutes at 90°C. The polymer could also be cleaved by cross-metathesis with an excess of 4-octene which gave, as the main product, 9-tridecenyl-7-undecenoate, thus confirming the structure assignment as indicated in Eq. (62). The unsaturated lactone was also copolymerized with cyclooctene, 1,5-cyclooctadiene, and cyclopentene under the previously stated conditions to afford linear copolymers which were high molecular weight, unsaturated, rubbery polyesters (110).

Use of $\text{WCl}_6/(\text{CH}_3)_4\text{Sn}$ permitted the synthesis of relatively high molecular weight polyalkylenes containing pendant ester groups (111). Thus, monomers containing cyclopropane groups prepared by the reaction of ethyl diazoacetate with 1,5-cyclooctadiene, 1,5,9-*cis,trans,trans*-cyclo-dodecatriene, and norbornadiene, respectively, undergo polymerization [Eqs. (63)-(65)]. Molecular weights and conversions appeared to increase

with increasing ring strain in the monomer. It is interesting to note that the integrity of the cyclopropane groups was not disturbed.

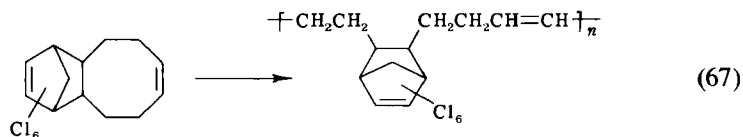


The presence of halogen atoms appears to exert little, if any, effect on catalyst activity, but it can influence the course of the metathesis reaction. Vinylic halides are unreactive, as exemplified by the ring-opening polymerization of 1-chloro-1,5-cyclooctadiene, which afforded a perfectly alternating copolymer of butadiene and chloroprene (112) via polymerization exclusively through the unsubstituted double bond.



Retention of the *cis* configuration at the halogen-bearing double bond confirmed the lack of reactivity at this position.

The Diels-Alder adduct of 1,5-cyclooctadiene with hexachlorocyclopentadiene was homopolymerized or copolymerized (113) with cyclic olefins using tungsten halide salts with either organoaluminum or organotin cocatalyst to give thermally stable flame- and oil-resistant polymers.



In summary, the metathesis of olefins substituted with polar functional

groups is still in its infancy but promises to be a very fruitful area for applications of metathesis to synthetic organic chemistry.

VI

CONCLUSION

In the March 3, 1978 issue of *Chemical and Engineering News*, a feature article examined activities at the forefront of inorganic chemistry. On olefin metathesis, the article states: "How the organometallic complexes affect the reaction is just now becoming well understood." In our review, the accent has been on aspects of olefin metathesis which are not well understood, with the hope that this will stimulate new and original work related to this remarkable reaction.

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